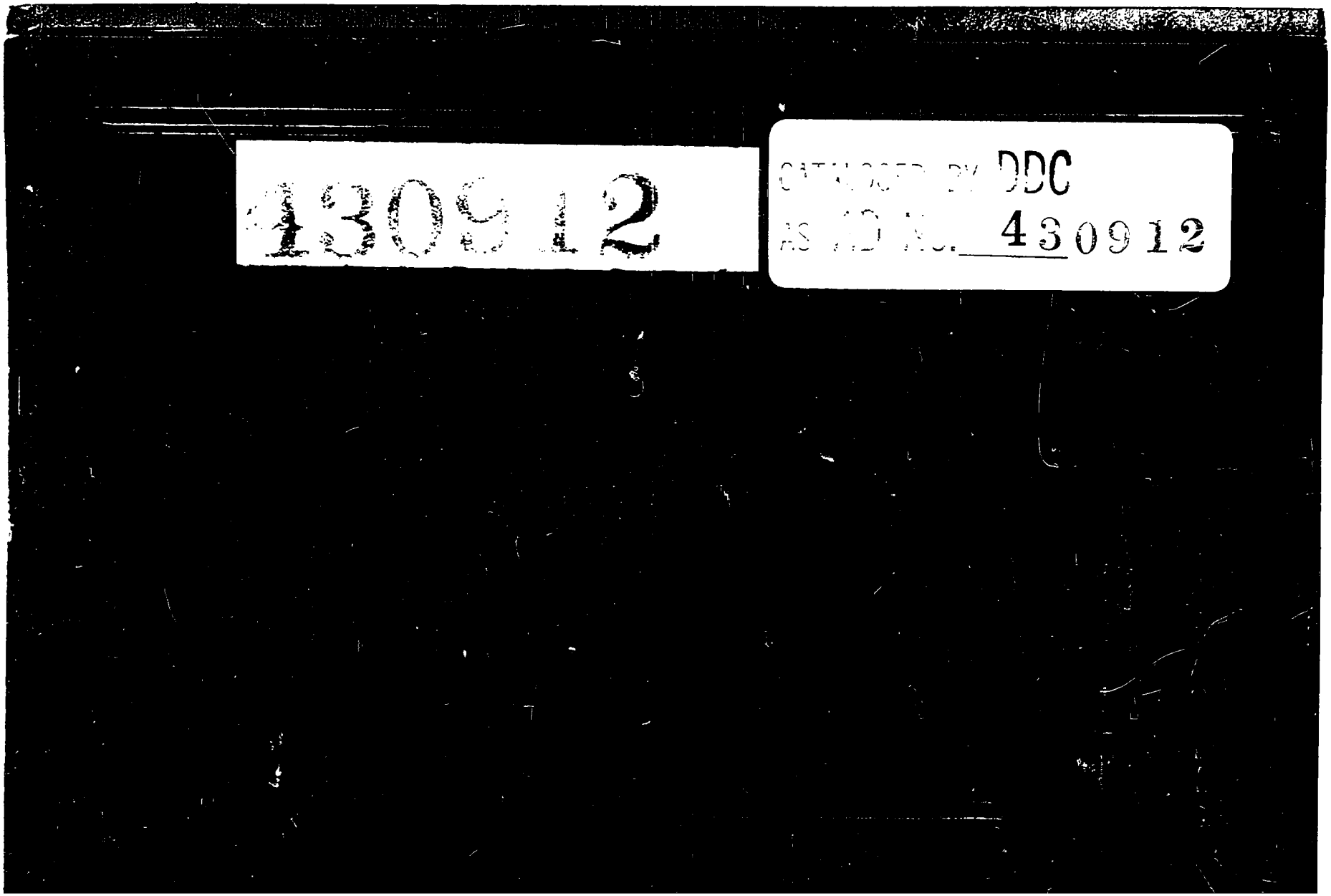

INORGANIC DIELECTRICS RESEARCH

FINAL REPORT

U. S. Army Electronics Research and Development Laboratory

Contract NO. DA-36-039-sc-89141

November 1, 1961 to October 31, 1963

File No. 01007-PM-62-93-93

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P R E F A C E

The information reported herein covers a two year contract period. The phase entitled "Low Loss Boron Nitride Ceramic Dielectrics" was terminated after the first year.

The project is continuing under Contract No. DA-36-039-AMC-03404(E). Four phases are being studied. "Hot Extrusion of Ferroelectric Ceramics" and "Low Loss Ceramics" are continuing essentially as set up under the previous contract, the dielectric constant requirements have been increased to 80 and higher for the latter phase. The emphasis in "Devitrified Ferroelectric Ceramics" in the last contract was on making a powdered glass of pure barium titanate, from which specimens were made conventionally, and during a subsequent firing the crystalline phase formed. The emphais has been shifted to more complex glass compositions in which barium titanate will be devitrified but in larger specimens of glass rather than in specimens formed from powdered glass. The emphasis in "Transparent Polycrystalline Ceramics" has been shifted from linear dielectrics to ferroelectrics. The title has been changed to "Structure Studies of High Density Polycrystalline Ceramics" and barium titanate is the first material to be studied.

A paper entitled "Similarities in the Impact Behavior of Glasses and Polycrystalline Ceramics," by C. J. Phillips and S. DiVita has been published in The American Ceramic Society Bulletin, Vol. 42, No. 11, November, 1963.

The following papers have been presented at various American Ceramic Society Meetings:

1. Properties of Several Boron Phosphate-Silica Devitrified Compositions.

2. Structural Analysis of a Boron Phosphate Silica Glass and Its Physical Properties.

3. Devitrified Pure Barium Titanate Dielectrics.

4. Electrical and Structural Characteristics of Devitrified Barium Titanate.

5. Precracted Raw Materials.

A two hour review of theoretical program was presented before the Advisory Group on Electronic Devices, AGED on November 14, 1962.

A Patent #3,084,053 entitled "Ceramic Materials and Methods For Making Same" was granted and is dated April 2, 1963.

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Part I

DEVITRIFICATION OF $BaTiO_3$

Abstract

A ceramic has been produced of very fine crystal size (0.2 - 0.5μ) by devitrification from a finely powdered barium titanate glass which was fabricated conventionally. This results in producing a barium titanate crystalline phase which is more tetragonal, and in increasing the Curie temperature to approximately 150°C.

Part II

LOW LOSS BORON NITRIDE CERAMIC DIELECTRICS

Abstract

An evaluation of industrial hot pressed boron nitride reveals that it is both porous and soluble which causes deterioration of its electrical properties under high humidity conditions. A procedure has been evolved to produce hot-pressible boron nitride and the parameters established to attain optimum properties. Boron nitride thus produced is slightly better than the industrial material evaluated. However commercial pyrolytic BN of excellent quality is now available which is not affected by moisture.

Part III

TRANSPARENT POLYCRYSTALLINE CERAMICS

Abstract

Section A - Anisotropic Crystalline Phases

Alumina bodies were fired in four atmospheres; hydrogen, oxygen, argon or vacuum. A two-fire procedure was used with the same or different atmosphere in each of the two fires. Fired specimens were evaluated for density, moisture absorption, total porosity and translucency. Microscopic methods were used to determine grain and pore size. Specimens fired in vacuum exhibited the best results and argon the poorest. All specimens exhibited lower transparency than "Lucalox."

Section B - Isotropic Crystalline Phases

A higher degree of transparency should be possible with an isotropic crystalline phase than with an anisotropic one. Spinel, that is magnesium aluminate, was selected for study. A pre-reacting technique was devised to attain excellent uniformity in mixing of the raw ingredients. Specimens were prepared and fired to an average degree of uniformity. The next step would have been to determine the firing parameters (temperatures, times, atmospheres) necessary to attain theoretical density.

Part IV

LANTHANUM ALUMINO SILICATE DIELECTRICS

Abstract

The object of this phase is the development of low loss ceramics with dielectric constants in the range of 12 to 15. The lanthana-alumina-silica system was selected for study. All the techniques investigated to mature these compositions are presented with an evaluation of each technique. Problems encountered are also discussed. Electrical properties of composition within the system are given. Correlations of these properties with regard to crystal and glass content, crystalline types and porosity are also presented.

Compositions which do not contain glass and located within the systems MgO-ZrO$_2$-TiO$_2$ and CaO-SiO$_2$ were evaluated for electrical properties. The procedures and results are presented.

Part V

HOT EXTRUSION

Abstract

A brief review of the work on hot extrusion of ceramic materials is presented, including the equipment and procedures used. The importance of coextrusion can design is discussed and illustrated.

Final Report - Part I

DEVITRIFICATION OF $BaTiO_3$

Introduction

Barium titanate is a ferroelectric ceramic which is characterized by a room temperature dielectric constant of approximately 1200 that increases slowly to approximately 110°C. Above this temperature the dielectric constant rises sharply to a maximum of approximately 8000 at 120°C, this drops off rapidly to some low value in the range of 100 above this temperature. At its Curie temperature (120°C) the barium titanate inverts from the tetragonal crystalline phase which is ferroelectric to the cubic phase where it became a linear dielectric. Solid solutions of this compound with other compounds such as strontium titanate and minor additions of other compounds such as the alkaline earths titanates tend to modify this overall effect by lowering the Curie temperature or having the effect take place more gradually over a wide temperature range. These approaches are utilized in industrial dielectrics, however, these effects are limited. The Curie temperature can be increased by making solid solutions with lead titanate, however, many limitations are involved such as stichometry due to the high vapor pressure of lead, etc. The more

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advantageous approach is to increase the Curie temperature or to eliminate it entirely as this would allow for high working temperatures.

About 10 years ago Anliker, Brugger, and Kanzig[1] noted that with very finely divided loose powders of barium titanate, the temperatures at which the transition from the tetragonal to the cubic form took place, increased as the particle size decreased. This was determined by X-ray and electron diffraction methods. Many attempts have been made to make fired ceramics of very finely divided barium titanate however during firing the crystals grow quite rapidly and the relatively large size results in the Curie temperature being at 120°C. A plausible approach to the attainment of very small crystals in barium titanate ceramics is to devitrify and control crystallization from a glass, that is, a randomly oriented structure of pure $BaTiO_3$. Thus the object of this problem is to produce a glass of pure barium titanate, then to prepare specimens of the powdered glass which on subsequent firing will devitrify to small barium titanate crystals.

Procedure

Earlier efforts Progress Report No. 7, March 1 to June 1, 1960, to produce a pure barium titanate glass proved futile.

---

[1] M. Anliker, H. R. Brugger and W. Kanzig, Helv. Phys. Cecta 27 99 (1951).

Boric oxide additions at 9% and higher and later tellurium oxide at 8% and higher, resulted in attaining a glass which could be fritted in very small quantities. However the barium titanate resulting by devitrification was so diluted by the remaining glassy phase that the highest dielectric constant attained was 120.

Method for Producing $BaTiO_3$ Glass

A procedure was divised by which finely divided barium titanate could be fritted by the use of Metco Type 2D Thermo Spray Gun. The complete details of this effort appears in Progress Report No. 6, February 1 to May 1, 1963. The gun was so located as to spray downward at an angle of 30° with the horizontal into a reservior of distilled water with the nozzle of the gun being 6" from the surface of the water. The finely divided raw barium titanate had to be made into specimens, fired to approximately 2200°F, thermal shoched and reduced to a controlled finely divided powder which would pass 325 mesh. Too many fines were detrimental. This procedure and a narrow particle size distribution was necessary for the material to flow through the gun. Further the maximum size of this material was such that the particle would be melted through and quenched completely through on entering the water so as to result in a randomly oriented or glass structure. Very fine particles would cause the gun

to clog and also the mass of the individual particles would not be great enough to enter the water. This procedure resulted in perfectly spherical particles of glass which were isotropic petrographically, and exhibited no structure by X-ray analysis. Two commercially available sources of barium titanate were used: Capacitor grade and chemically pure grade. Both are produced by the Titanium Alloy Manufacturing Division of National Lead Company. The first is approximately 97% barium titanate which the latter is 99.9+%.

Method for Producing Test Specimens

The spherical $BaTiO_3$ glass particles resulted in rather low green and fired bulk density when evaluated as prepared specimens. To attain better packing the spheres were ground in an automatic alumina mortar and pestle apparatus for a minimum period of time. A small amount of water was used as a binder and the specimens were pressed at 1/2 inch diameter by apprximately .060" thick at 10,000 psi. The specimens were fired in a platinum wound electric furnace, first in air and later in oxygen. The latter atmosphere gave the highest fired bulk densities.

Result

The properties of solid sintered $BaTiO_3$, $BaTiO_3$ glass and devitrified bodies made from the $BaTiO_3$ glass are presented in Table 1 on page 9. Electrical data is presented graphically in Figures 1, 2A, 2B on pages 6 through 8.

Petrographic analysis, X-ray analysis and other methods prove that $BaTiO_3$ glass is formed by flamespraying and rapid quenching. This glass has an index of refraction of 2.25 which is appreciably lower than the crystalline phase at 2.40. Its true density as determined by the pycrometer method is 4.799 which is much lower than the crystalline phase which is 6.012. The dielectric constant of the glass is approximately 70 until approximately 180°C at which temperature it increases radically, however this is not a Curie temperature. No hysteresis is exhibited by the glass. From this it can be concluded that the glass is not ferroelectric.

The power factor is 0.03. Devitrification takes place in the powdered glass spheres between 450 and 750°C and the body matures at 1310°C.

The true density of the devitrified body is 5.65. This is considerably lower than that of $BaTiO_3$ which was determined to be 6.012. This is due to the presence of 33.0% by volume of the compounds $BaTi_2O_5$ and $BaTi_3O_7$. The true density of the devitrified $BaTiO_3$ within the body is 6.022 and is considerably greater than that of the compound prepared normally as noted above. This is due to an increase in the lattice

Figure 1

DIELECTRIC CONSTANT vs. TEMPERATURE

FOR SOLID SINTERED AND DEVITRIFIED BARIUM TITANATE

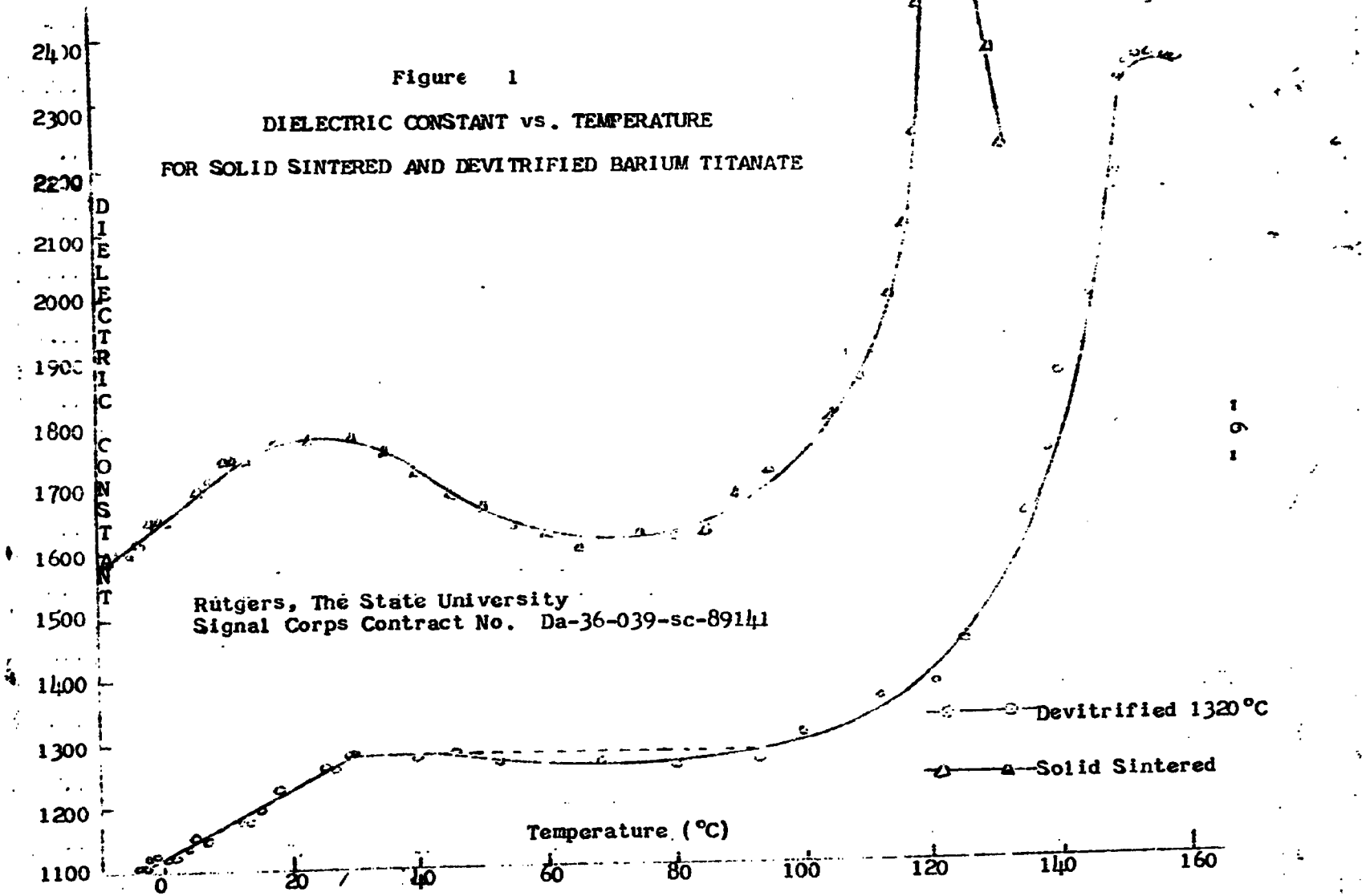

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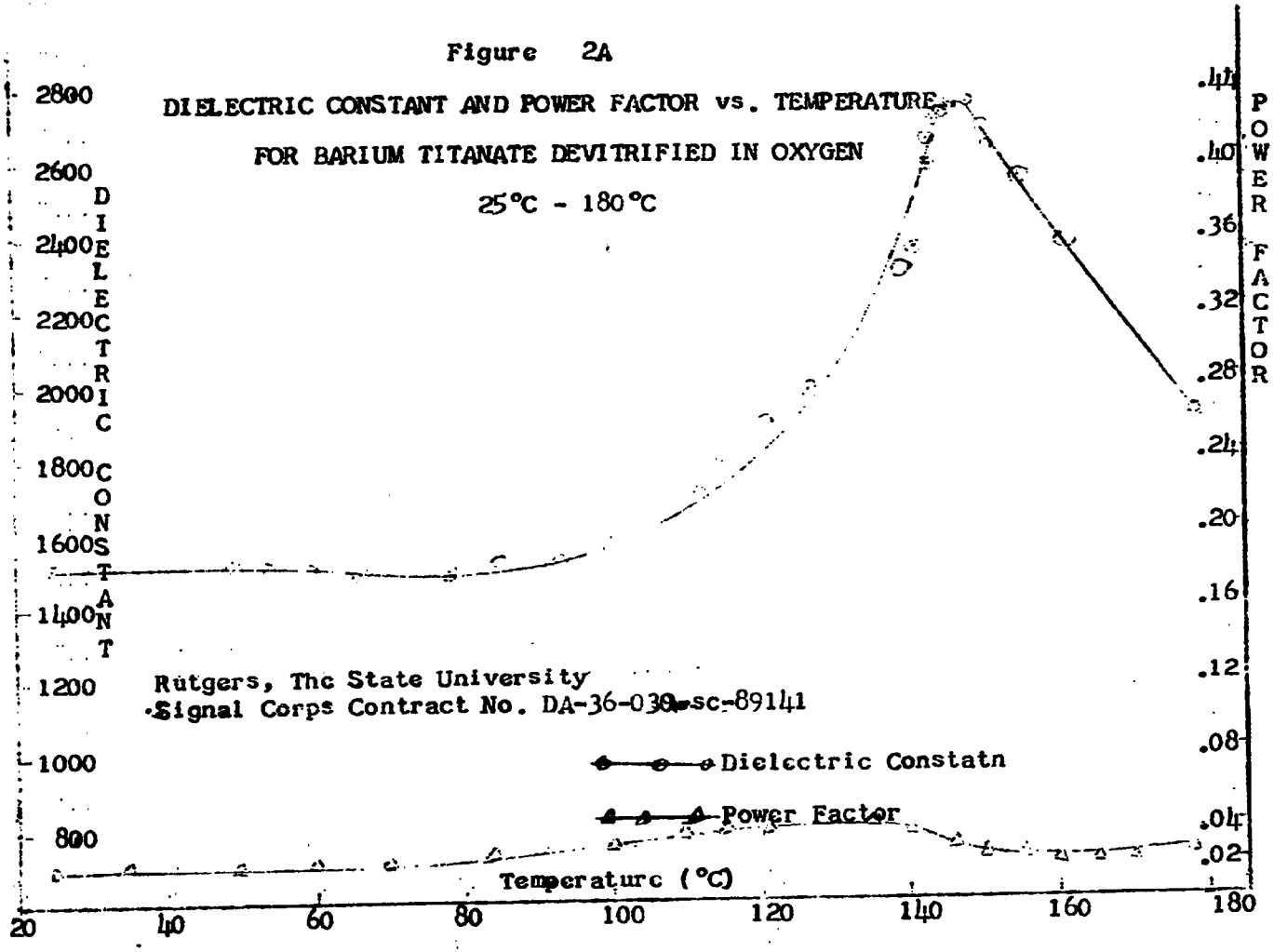
Figure 2A


DIELECTRIC CONSTANT AND POWER FACTOR vs. TEMPERATURE
FOR BARIUM TITANATE DEVITRIFIED IN OXYGEN
25°C - 180°C
DIELECTRIC CONSTANT
POWER FACTOR
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
.44
.40
.36
.32
.28
.24
.20
.16
.12
.08
.04
.02
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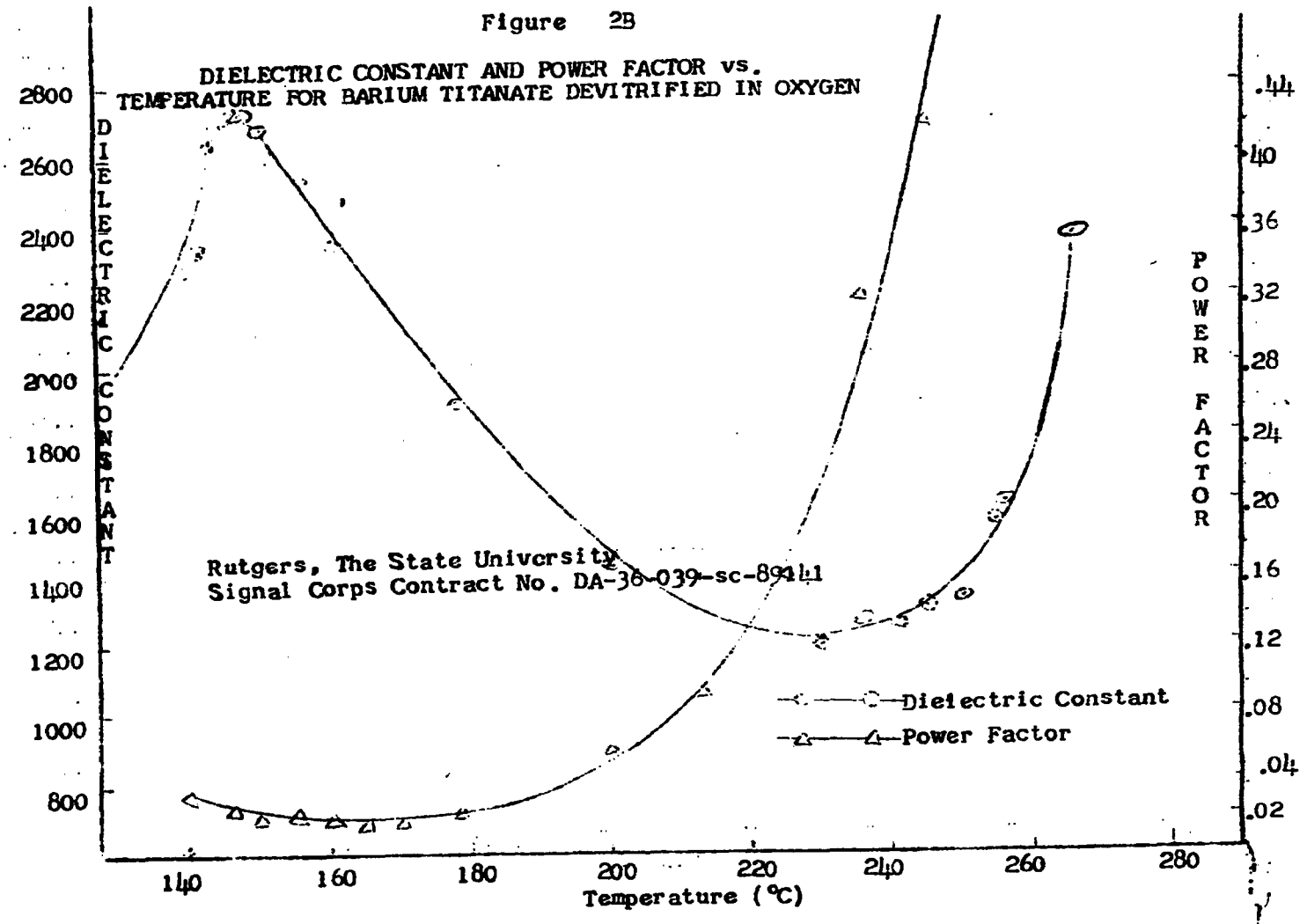
Dielectric Constatn
Power Factor
Temperature (°C)
20
40
60
80
100
120
140
160
180

Figure 2B


DIELECTRIC CONSTANT AND POWER FACTOR vs.
TEMPERATURE FOR BARIUM TITANATE DEVITRIFIED IN OXYGEN
DIELECTRIC CONSTANT
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
POWER FACTOR
.44
.40
.36
.32
.28
.24
.20
.16
.12
.08
.04
.02
140
160
180
200
220
240
260
280
Temperature (°C)
Rutgers, The State University
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Dielectric Constant
Power Factor

Table 1

Properties of $BaTiO_3$ Prepared by Several Methods

	Solid State Reacted	Glass	Devitrified Body
Index of Refraction	2.40	2.25	----
Density (gr/cc)			5.65[1]
True	6.012	4.799	(6.022)[2]
Bulk	5.50	-----	5.644
Dielectric Constant	1600[7]	70	1300[6]
Curie Temperature (°C)	120[7]		155[6]
Power Factor		0.03	.03[6]
Hysteresis		None	Yes
Lattice Constant			
a	3.994		3.988
c	4.028		4.043
Crystal size (μ)	10-80(10-50)[3]		0.2-0.5
Composition (fired)			
$BaTiO_3$	89.3%		62.0
Voids	19.7%		5.0
Other	-----		33.0[5]

1. As body
2. $BaTiO_3$ crystals in body.
3. Bulk of crystals within this range.
4. Fired in oxygen
5. These are $BaTi_4O_9$ and $BaTi_{20}O_{41}$.
6. See Figure 1 and/or 2A and 2B.

constants as noted in Table 1. Thus the barium titanate developed by devitrification is more tetragonal than the regular material and is undoubtedly responsible for some of the unusual electrical properties of the devitrified body. This higher density form may be due to its physical environment, strains, etc., within the body rather than being a new form. The bulk density as noted in the table is 5.64. This is the highest valve which was attained near the end of this effort by proper particle size reduction of the glass spheres which resulted in better packing, and by firing in oxygen. This quality of the best specimens approaches their true density. However, most results are reported on somewhat lower bulk density values and are reflected by the 5.0% void shown in the Table.

The Dielectric Constant vs. Temperature properties of the solid sintered and devitrified $BaTiO_3$ compositions are presented in Figure 1 on page 6. The solid sintered composition exhibits a typical curve for $BaTiO_3$ but at somewhat higher dielectric constants which is undoubtedly due to the purity of the starting material. The devitrified composition exhibits a more strait lined curve at a lower dielectric constant level. This latter effect is undoubtedly due to the presence of the subtitanates. However the Curie temperature of this latter material has been increased to approximately 150°C as compared to 120°C for the solid sintered material. Figure 2A and Figure 2B on pages 7 and 8 show the electrical

properties in the temperature range 20-200°C of the devitrified $BaTiO_3$ ceramic fired in oxygen. The power factor is approximately 0.03 to 180°C then increases very rapidly. The dielectric constant exhibits its Curie temperature at approximately 150°C, then decreases to 1200 at approximately 230°C, then increases very rapidly. Between room temperature and 100°C this composition exhibits a constant dielectric constant at 1500. Thus this type composition exhibits an increase in Curie temperature. The crystal size of the barium titanate ranges from 0.2-0.5 microns as compared to 10-80 microns for the solid sintered material. X-ray diffraction shows a gradual transition from the tetragonal to the cubic up to at least 180°C; hysteresis loops did not show paraelectric effects until 185°C; thermal expansion studies did not exhibit the break in the expansion in temperature curves of normal $BaTiO_3$ but rather a smooth gradual transion from the tetragonal to the cubic state. This overall behavior is associated with the presence of the very small $BaTiO_3$ crystals in the devitrified ceramics.

The presence of the subtitanates in the devitrified composition is due to a deficency of BaO in the composition. It was discovered that BaO was desolved from the glass on quenching into the distilled water. A separate study of this problem (Progress Report No. 7, May 1 - August 1, 1963) has resulted in no improvement. Undoubtedly the properties of a pure $BaTiO_3$ devitrified body would be appreciably improved if stichometric could be maintained.

Summary

A glass has been made out of barium titanate by the melting and rapid quenching of small particles of barium titanate. This has been accomplished by the flame-spray process and results in the formation of small isotropic spheres which are solid in nature. These have an expanded structure, as evidenced by their low density of 4.79 g/cc, and an index of refraction of 2.25. Their dielectric constant is in the vicinity of 70.

The glass has a crystallization temperature of 450°C. Differential thermal analysis reveals a large exothermic reaction between 450°C and 750°C.

The glass was fabricated into specimens and devitrified into crystalline ceramic bodies. The sintering of the spheres occurred between 1290 and 1300°C. Densification took place between 1300 and 1310°C, the maximum density being achieved at 1310°C.

The microstructure consists of two phases. The major phase consists of a submicroscopic crystalline mass of tetragonal $BaTiO_3$. The minor phase is a low density phase containing $BaTi_2O_5$ and $BaTi_3O_7$. These phases are present due to an excess titania content in the bodies. This arises from solubility of the baria in water during flame-spraying.

The crystals of barium titanate in the devitrified bodies are extremely small as compared to the size of those in a solid sintered composition of barium titanate fired under identical

conditions. The devitrified bodies have crystals which are 0.2 to 0.5 microns and less in size while the solid sintered composition has a crystal size distribution of 10 to 80 microns.

The lattice parameters, a and c, of the tetragonal barium titanate in the devitrified bodies were respectively 3.988 $\pm$ .004 and 4.043 $\pm$ .004. This gives a c/a ratio of 1.013 as compared to 1.010 for conventional barium titanate.

Because of poor packing of the glass spheres during fabrication due to their size distribution, the bulk densities of the fired body are quite low. This has been increased to a value comparable to that of the conventional solid sintered specimens by a pulverizing study of the glass particles prior to fabrication in order to obtain the optimum conditions for packing.

The Curie region of the devitrified bodies has been investigated by dielectric constant and hysteresis measurements, X-ray diffraction, thermal expansion and by optical means. These measurements reveal that the behavior is different from that of conventional barium titanate ceramics. The dielectric constant-temperature measurements show an increase from the usual 120° to 150°C. The hysteresis loops did not show a paraelectric transition until 185°C. X-ray diffraction showed a gradual transition from the tetragonal to the cubic structure up to at least 180°C. The thermal expansion curve does not show the discontinuity in the Curie region that the conventional bodies have. It is characterized

by an continuous curve which is smoothed out between 110 to 185°C. The optical study showed a progressive disappearance of birefringence over the temperature range of 120° to 185°C.

The room temperature dielectric constant of the bodies was 1280. The temperature dependence of the dielectric constant has been eliminated to a large extent in the devitrified bodies. The temperature coefficient is either zero or slightly negative. The Curie dielectric constant at 150°C is 2350. The maximum in the curve at the tetragonal to orthorhombic transition has been for all purposes eliminated in the devitrified bodies.

Devitrification of the bodies in an oxygen atmosphere improves the bulk density. This is reflected in the dielectric constant measurements.

Conclusions

1. A pure glass of barium titanate can be formed by the melting and rapid quenching of small particles.

2. Small crystals can be attained in the fired ceramic by devitrification of this glass.

3. The dielectric Curie transition has been shifted from the conventional 120°C to 150°C.

4. The shift is associated with the presence of small $BaTiO_3$ crystals in the devitrified ceramic.

Final Report - Part II

A STUDY OF BORON NITRIDE AND THE EFFECT OF ADDITIVES ON ITS HYGROSCOPICITY

Introduction

Hot pressed boron nitride, in solid and powder form, has a hexagonal crystalline structure similar to graphite. The solid form is a dense, strong body whose properties are directional because of the partial orientations of the plate-like crystals during fabrication. The most interesting features are the excellent electrical properties including high resistivity, low loss and high dielectric strength, even at elevated temperatures.

At low and moderate temperatures its resistivity approximates that of high alumina ceramics. Under conditions of very high relative humidity, its resistivity is somewhat lower. Its dielectric strength is in excess of 250 volts per mil. At high frequencies, the dielectric constant of boron nitride does not vary in the temperature range between 75° and 900°F. Tables I and II on page 16 show the electrical properties of industrial hot pressed boron nitride.

Along with its dielectric properties, its physical properties are also considered excellent. It has a hardness of 2 on the Mohs scale but its resistance to sandblast is equal to that of plate glass.

Boron nitride resists attack from most corrosive

materials, only water bearing compounds cause any effect on the material. Its machinability is equal to that of plastics.

Table 1

Electrical Properties

Frequency c/s	Dissipation Factor 75°F	600°F	900°F	Dielectric Constant 75°F	600°F	900°F
			A Direction			
10^2	0.00103	0.032	1.0	4.15	4.4	9.0
10^4	0.00042	0.0043	0.1	4.15	---	4.5
10^6	0.00020	0.0012	0.0056	4.15	---	4.25
10^8	0.000095	------	------	4.15	---	4.15
			B Direction			
10^{10}	0.0003	0.0004	0.0005	4.80	---	4.80

A Direction - Measured parallel to molding pressure

B Direction - Measured perpendicular to molding pressure

Table 2

Resistivity vs. Humidity

R. H.%	Resistivity at R. T. (ohm-inches)
20	3.9×10^{11}
50	2.9×10^{10}
90	1.9×10^{9}

From Tables I and II it is obvious that the electrical properties are excellent and are in the ultra low range, however, actual use of this material indicates that it is markedly affected by moisture with the electrical properties deteriorating quite readily with high humidity.

It is obvious that boron nitride ceramics have many desirable properties and if the effect of moisture could be eliminated or overcome the material could be used advantageously. Thus, the object of this phase of the effort is to determine the fundamentals and procedures by which moisture resistanct boron nitride can be made. The details of this work may be found in Progress Report No. 7, May 1 to August 1, 1963

Procedure and Results

Boron nitride ceramics cannot be prepared by sintering. The crystalline phase starts to dissociate above 1600°F. Attempts were made to sinter in the presence of a low temperature glass however advantageous properties are so diluted that the final product was of little significance. Further only a very few glasses would wet the crystalline phase which was a very limiting factor. Thus hot pressing is the only forming or fabricating method that can be used. It was soon learned that the powdered boron nitride supplied industrially could not be hot pressed. Further neither of the two firms supplying this material at the time this work was being done would supply a hot pressible material - they would supply only hot pressed blanks from which specimens could be machined or the powdered material which would not hot press. So it became necessary to learn how to prepare boron nitride that would hot press.

A. Properties of Industrial Hot Pressed Boron Nitride

Several small batches of industrially supplied hot pressed boron nitride were purchased. The moisture absorption was as high as 4.7%. Specimens were machined and the power factor and dielectric constant determined at several levels of relative humidity as noted in Table 3 below.

Table 3

Electrical Properties of Industrial BN vs. Relative Humidity

Humidity	Power Factor	Dielectric Constant
100%	Not measureable	----
93%	.4200	3.1
85%	.2100	6.3
73%	.0975	6.8
67%	.0190	7.8
44%	.0021	4.6
34%	.0015	----
Dry	.0009	5.15

The effect of 100% Relative Humidity vs. Time on Surface Resistivity is shown in Table 4 below.

Table 4

Surface Resistivity vs. Time at 100% Relative Humidity

Time (Minutes)	Surface Resistivity (ohms)
10	2×10^4
20	4×10^3

Time (Minutes	Surface Resistivity (ohms)
30	9×10^8
40	3×10^8
50	17×10^8
60	6×10^1
70	3.5×10^1
80	2.5×10^1
90	1.9×10^1
100	1.6×10^1
110	1.2×10^1
120	1.0×10^1

At 75 and 50% relative humidity the resistivity is greater than 10^{18} ohms.

Further it was proven that boric oxide is present in the boron nitride and can be dissolved from it. Thus this hot pressed boron nitride is quite porous and soluble B_2O_3 is present, and both factors contribute to the loss of electrical properties under high humidity conditions.

B. Hot Pressed Boron Nitride Made With Industrial Powdered BN

As noted above industry would not supply hot-pressible boron nitride so it became necessary to learn how to make it. The first phase was to attempt to use pure industrial powdered

BN. A study of the literature including numerous patents revealed that at least 2.5% B_2O_3 and some CaO was necessary to hot press boron nitride. The composition which evolved experimentally is as follows 83% pure BN, 7% B_2O_3 and 10% $Ca_3(PO_4)_2$. This agrees with the patent literature. However this composition exhibited 22% moisture absorptions. A series of additives, selected for specific reasons, were made to the above composition and several others. The moisture absorption was decreased to 14.3%.

C. Hot Pressed BN Made From Laboratory Prepared Material

Since the lowest moisture absorption attained using industrial powdered BN was 14.3% it became necessary to learn how to make the hot-pressible BN. The patent literature revealed that to form this phase, it was necessary to first form a mixture of boramides $(BNH_2)^3$ and borimides $B_2(NH)_3$. This mixture converts to BN during hot pressing. The starting materials are two gasses namely boron trichloride and ammonia. The two gasses were allowed to flow at the proper rates into an enclosed porcelain container when they reacted to form a white, fluffy, snow-like solid. This material was then heated to 600°C in an atmosphere of O_2 and H_2 to drive off volitile impurities and form the mixture of boromides and borimides. The material was then ready for hot pressing during which it was converted to BN. This hot pressed material had a moisture absorption of 30%.

A study of the hot pressing variable revealed that 1850°C and 3000 psi were the optimum temperature and pressure respectively which resulted in a moisture absorption of 3% as compared to 4% for the industrial material. A study of additives at 0, 1 and 5 mole per cent of a number of selected additives revealed that all increased the moisture absorption.

Pyrolytic Boron Nitride

Boron nitride ceramics are also formed by pyrolytic depositions and is industrially available. This form is much more oriented than the hot pressed material. It is essentially pure and definetely does not contain B_2O_3. Its moisture absorption was found to be 0.3% as compared to 4.7% for the commercially hot pressed material. The physical and electrical properties of both types of BN are similar.

Summary

Hot pressed boron nitride has many advantageous engineering properties, especially electrical properties including high resistivity, low loss and high dielectric strength, even at high temperatures. However they tend to deteriorate under high humidity. The object of this effort is to attempt to overcome this short coming.

A study of industrial hot pressed BN revealed that it is porous, up to 4.7% moisture absorption and contains soluble boric oxide. These conditions result in the deterioration of the electrical properties.

In order to attempt to remedy these short comings a program was pursued to determine the compositions necessary for hot pressing. This was determined from the literature and experimentally. A phase of the study entailed the addition in small quantity of selected additives to assest during hot pressing. The best quality attained was 22% moisture absorption. Thus the boron nitride as supplied was not hot hot-pressible nor could it be made so by additives. Industry would not supply hot-pressible material so it became necessary to learn how to prepare it. This was accomplished and after a study of the hot-pressing variables, the best quality produced exhibited 3% moisture absorption; that available from industry exhibited 4+%. Selected additives showed no improvements.

Final Report - Part III

TRANSPARENT POLYCRYSTALLINE CERAMICS

Section A - Anisotropic Crystalline Phases

Introduction

The objective of this phase of the program is the development of a highly translucent or transparent polycrystalline ceramic body. The material should have extremely high density (within 0.5% of true density), high purity, small crystalline size, and improved homogeneity and grain boundary structure.

Cubic crystalline phases, such as magnesia and spinel, must be ultimately utilized as anisotropy will be eliminated with these materials, producing optimum results. However for this phase of the work it was decided to use alumina principally because of its importance in dielectrics and to attempt to clarify some of the details in its preparation as a transparent material.

Method of Approach

In this investigation, compacts of alumina were fired according to the general procedure described for the manu-

fracture of General Electric's Lucalox, a commerical, translucent alumina body. This body is prepared of substantially pure, finely-divided alumina, containing 0.25% MgO to inhibit grain-growth. A two-fire procedure is used, the first to remove gas-containing pores, the second to induce transparency. A hydrogen atmosphere is used. The first firing is accomplished at a temperature of from 1650°C to 1750°C, for a period of from 50 to 300 minutes; the second at a temperature of from 1850°C, to 1950°C, for a period of not less than 15 minutes. The principal difference in this investigation is that a combination of atmospheres was to be employed. The specific procedure established is as follows: the samples were first fired to 1700°C for 100 minutes in one of four atmospheres: hydrogen, oxygen, argon or vacuum. Then, the samples were refired to 1900°C in the same or a different atmosphere, for periods of 15, 60, and 300 minutes. For example, twelve specimens were fired in argon at 1700°C. Then, groups of three were refired at the higher temperature in each of the four atmospheres respectively listed above, one each at each of the three time periods listed above. This proceedure was repeated for all atmospheres in the first fire.

Procedure

The materials used in this study were "Linde A" Alumina as the source of Al_2O_3, and Baker's magnesium nitrate crystals as the source of MgO.

The furnace is an atmosphere induction furnace and is described in detail in Progress Report No. 4, August 1, 1962 to November 1, 1962. Specimens were fabricated in the following way: One hundred gram batches were weighed out on an analytical balance and placed in a glass jar. Magnesium nitrate solution was added to give the correct MgO content, and enough water to form a slurry. The jar was sealed and agitated. The slurry was then poured into a pan, covered with alumina foil, dried, and then ground in a mortar with a pestle. Discs 5/8 inch in diameter and 1/4 inch thick were pressed at 50,000 psi using a hydraulic press.

Bulk densities and moisture absorptions were determined by the water immersion technique. Transparency measurements were made using the Lumetron 402-E Colorimeter. Color filters, each isolating wave banas 30 millimicrons wide, were used to obtain spectral transmission curves in the visible range for those specimens translucent enough to give readings. The specimens were not polished or otherwise specially prepared for these measurements, but were tested just as fabricated and fired. Polished specimens were used for microscopic examination. They were polished with diamond grit paste on an "automet" polishing machine. To bring out the grain structure, they were etched for 75 minutes with concentrated hydrofluoric acid. The following data were determined: maximum and minimum grain size; average grain size; average size of pores; location of pores.

Result

Density results are shown graphically in Figures 1 through 4 on pages 27 through 30. Density increases from the first to the second fire and is shown in two ways. Figures 1 and 2 show the effect of second fire in all atmospheres respectively on all specimens having the same first fire atmosphere while in Figures 3 and 4 are plotted the densification rate for those specimens having the same atmosphere in the second firing and the several atmospheres respectively during the first firing.

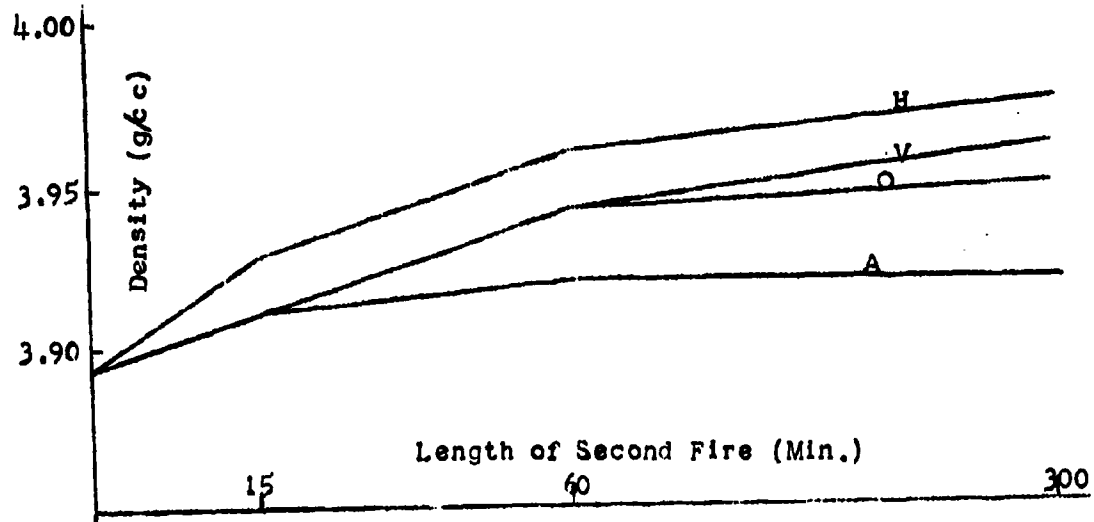
Initial (first-fire) densities were lowest with argon, averaging only 3.77 g/cc. The densities after the first fire were much higher with the other three atmospheres, averaging 3.89 g/cc or about 97.5% of theoretical density, with hydrogen, oxygen and vacuum. All specimens increased in density the second fire. Those samples fired initially in argon showed the highest increase during the second fire, but this was due to their having the lowest single-fire densities. In general, those specimens having the lowest single-fire densities showed the largest increases from first to second fire.

It appears that the first fire is the important one, in that it seems to be the limiting factor in densification. In other words, the degree of densification possible in the second fire is determined by that attained in the first fire.

Figure 1

DENSITY vs. LENGTH OF SECOND FIRE

A. Specimens Having Hydrogen First Fire



B. Specimens Having Argon First Fire

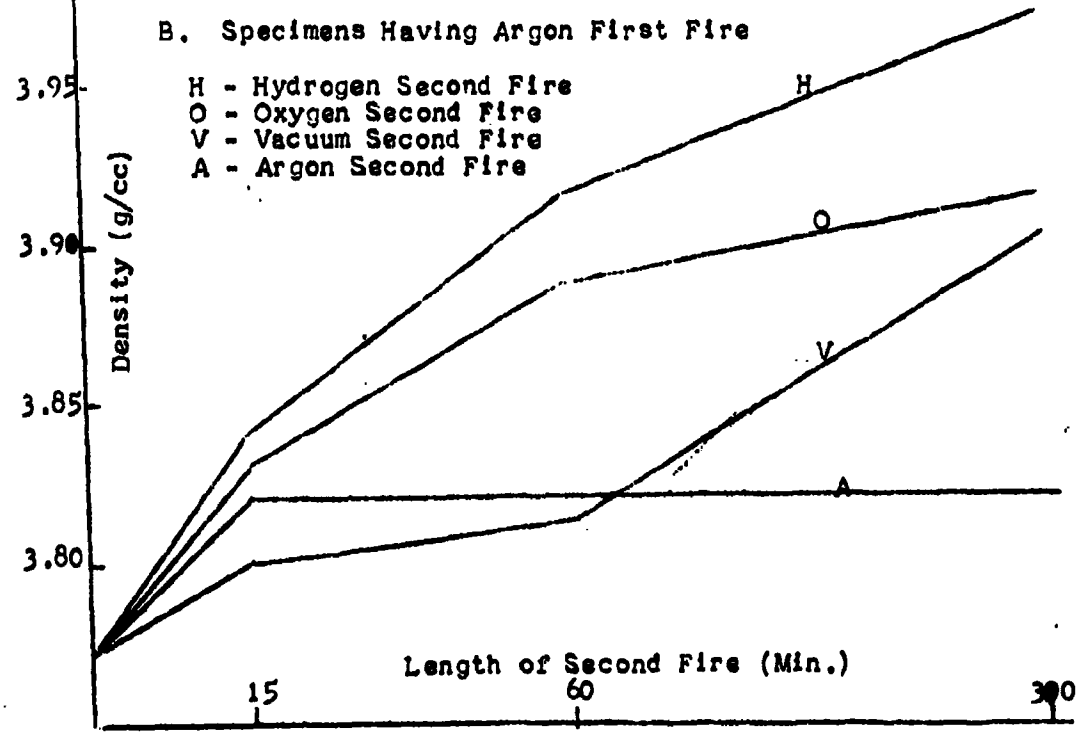


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Figure 2

DENSITY vs. LENGTH OF SECOND FIRE

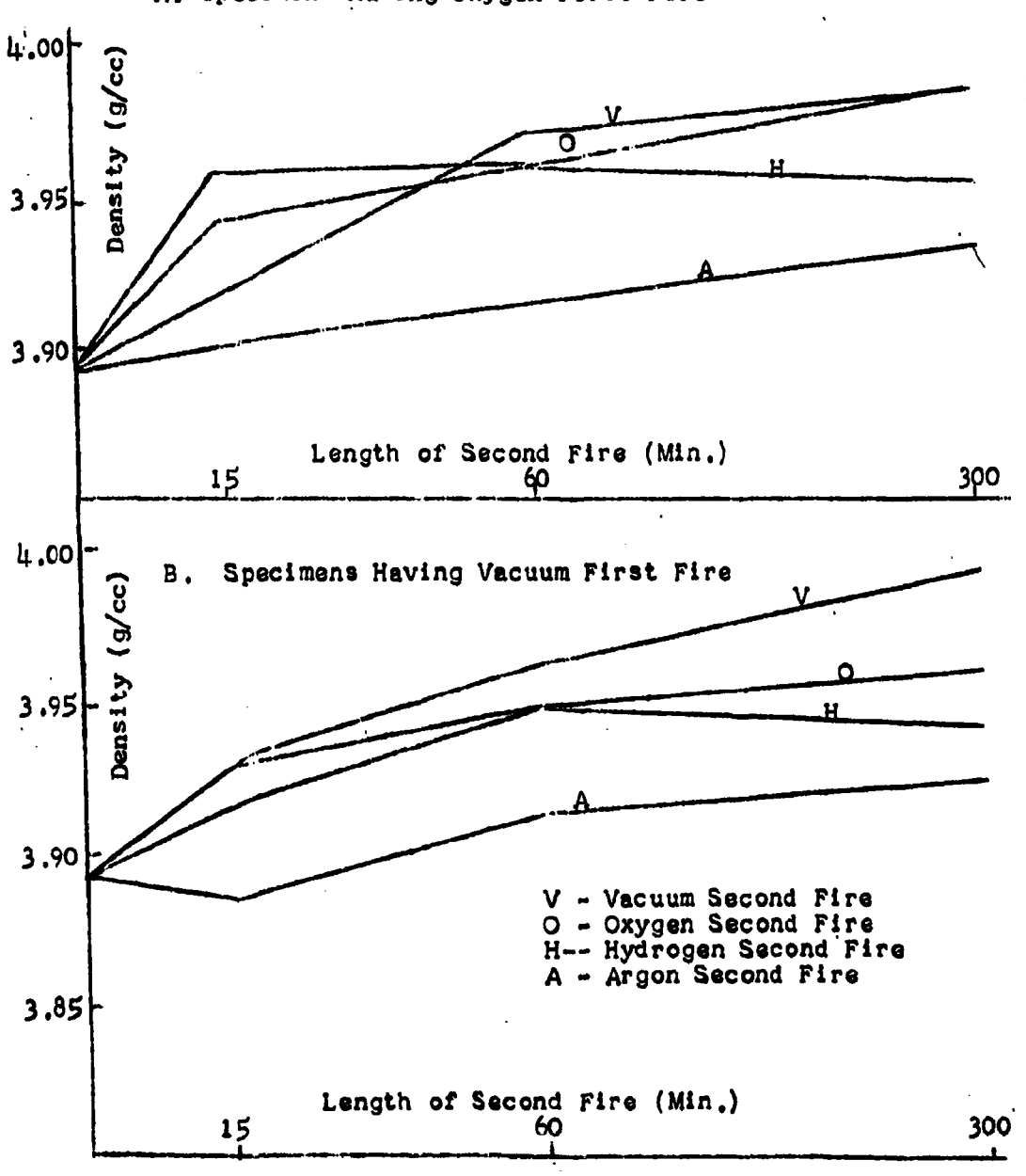

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Figure 3

DENSITY vs. LENGTH OF SECOND FIRE

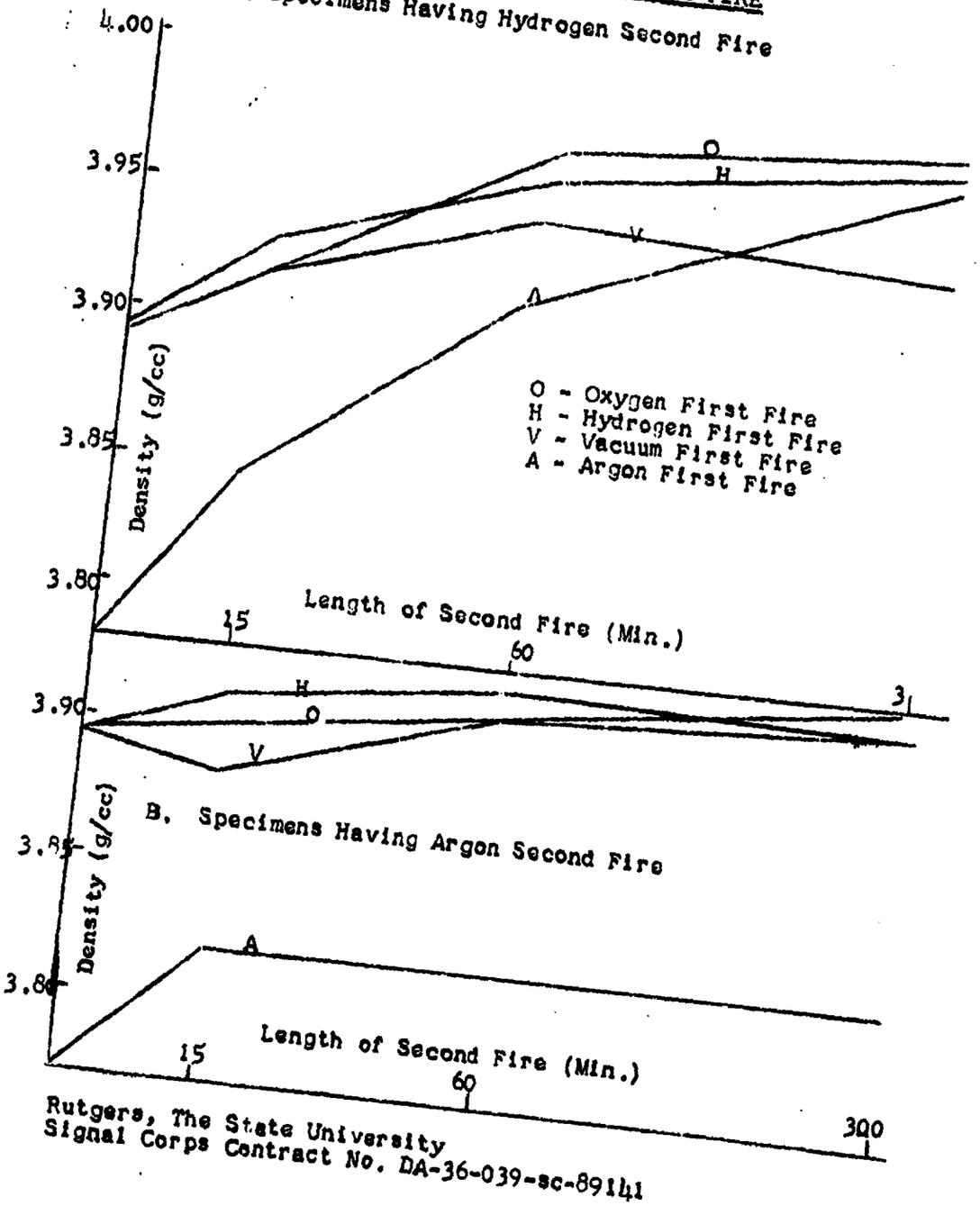

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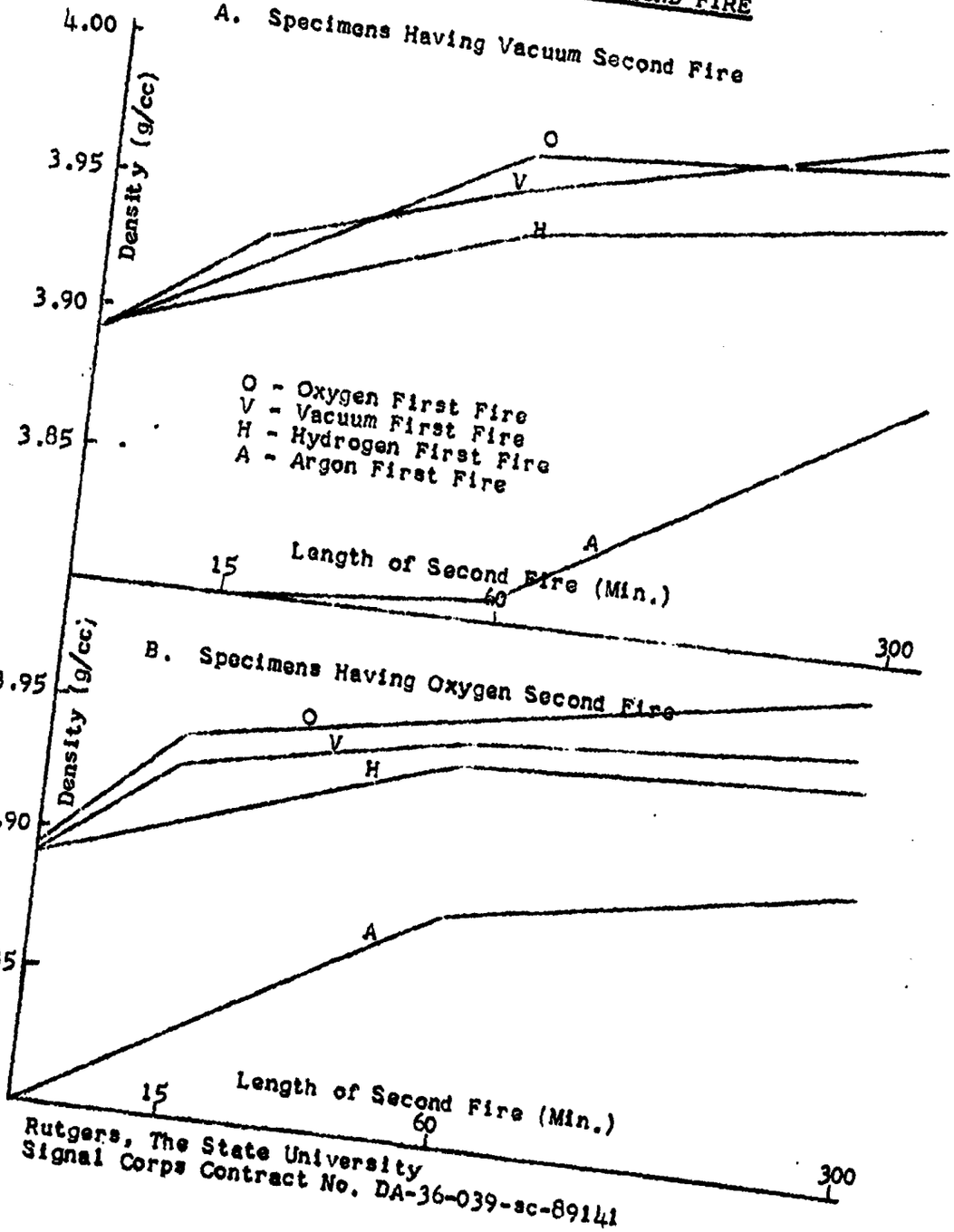
Figure 4

DENSITY vs. LENGTH OF SECOND FIRE



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Those samples fired initially in argon remained lower in density than those fired in the other two atmospheres and vacuum, even though they exhibited a greater percentage increase in density from first to second fire.

The graphs show that hydrogen, oxygen, and vacuum behave similarly in their effect on densification. The specimens fired in each of the three show similar initial densities; while the rate of densification in the second fire is about the same whether the specimen was fired in the same or different atmosphere. In all cases, theoretical density was approached in the five hour fire in hydrogen, oxygen and vacuum for those specimens fired intially in any of these three atmospheres.

Those specimens fired in argon only exhibited lower densities than for the other specimens in all second-fire atmospheres. Only after the five hour fire in hydrogen did any of these specimens approach the densities obtained by the other first fire atmospheres. In all cases, there appeared to be a limiting density when the atmosphere for the second fire was argon.

Mature bodies with 0.0% moisture absorption were obtained only when the total porosity was reduced to 1.0% or less.

Translucency Measurements

Only a few specimens fired under a rather limited set of conditions as shown in Table 1 below exhibited a sufficient

degree of translucency to obtain measurements on the colorimeter. All specimens, except those for which the first firing atmosphere was argon, were translucent by visual inspection, that is, when the specimen was held up to the light and a finger placed behind the specimen, the shadow of the finger could be seen through the specimen. Although in theory the colorimeter will give all readings from 0 to 100%, there appears to be a minimum, or threshold value, below which it is not sensitive enough to give readings. This threshold value appears to be in the order of 30%. In other words, unless the specimen passes at least 30% of the light, no readings could be obtained. Translucency measurements for these specimens are given in Table 1 below. Also included are the values for the commercial alumina.

Table 1

Light Transmission, %

Filter #	Lucalox	A	B	C	D
390	70	35	40	45	45
420	70	40	45	50	50
465	70	40	45	50	50
515	75	45	45	50	55
550	65	40	40	45	50
575	55	30	35	40	40
595	50	30	35	35	35
620	40	--	--	--	--
660	30	--	--	--	--

Figure 5

GRAIN SIZE .. vs. LENGTH OF SECOND FIRE

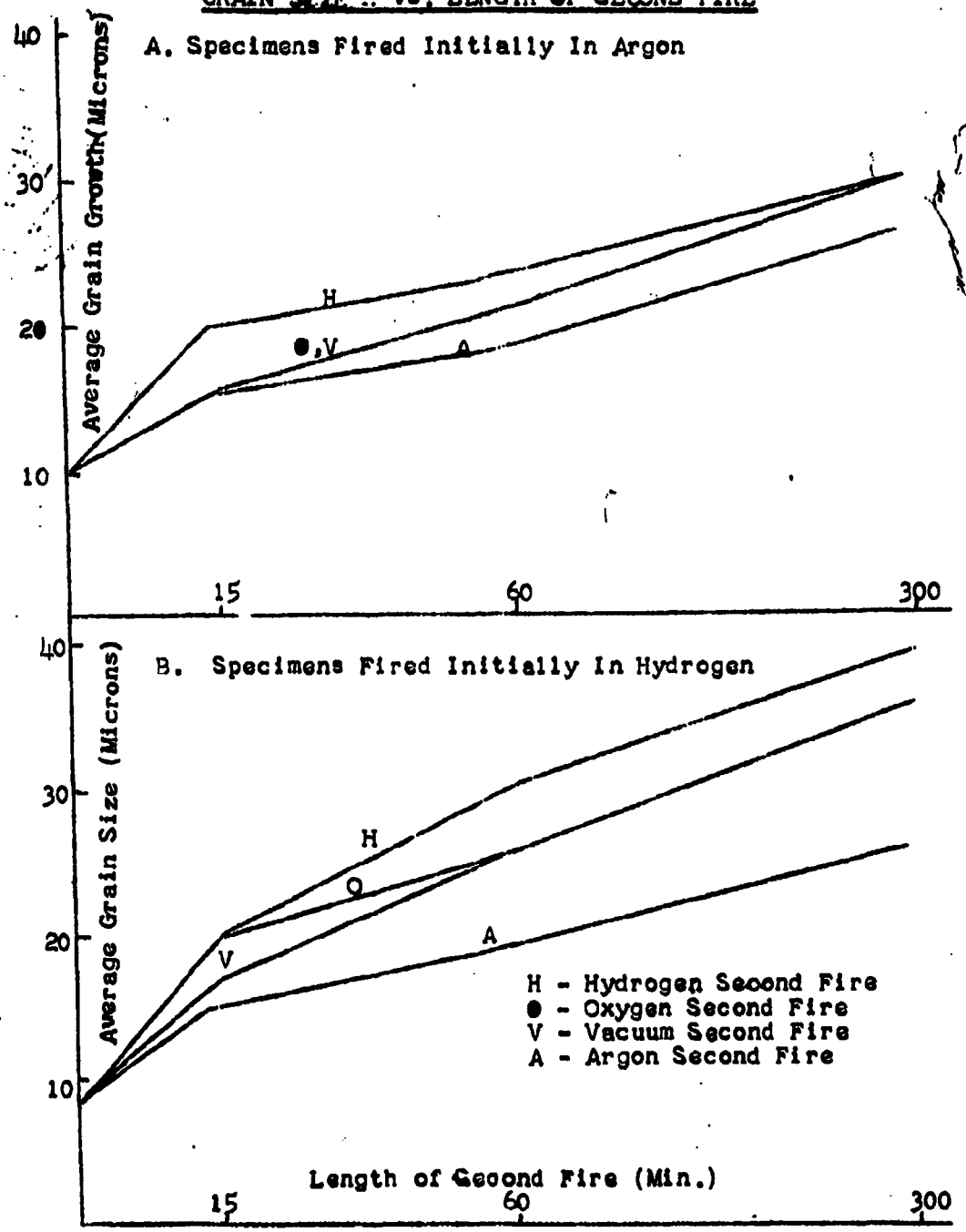

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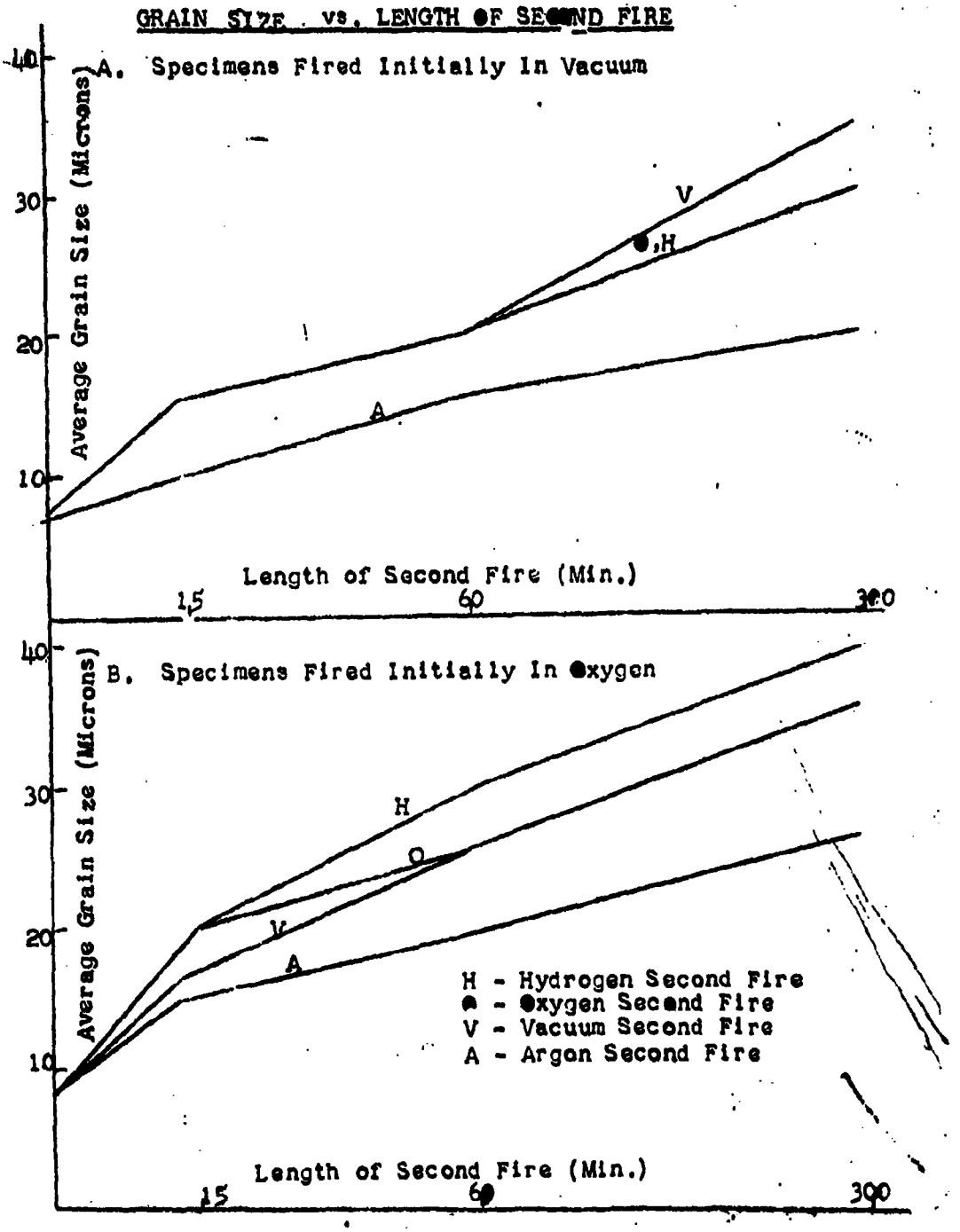
Figure 6

GRAIN SIZE vs. LENGTH OF SECOND FIRE



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Heat Treatment and Environment

1st Fire	---	0^a	V[1]	V	V
2nd Fire	---	V[1]	0^a	V	V
Time of 2nd Fire(min.)	---	300	300	60	300

1 Fired in Vacuum

Microscopic Examination

Grain Growth vs. Length of Second Fire of all firing atmosphere combinations studied are shown in Figures 5 and 6 on pages 33 and 34. For comparison, the grain sizes for Lucalox are as follows: Maximum grain size, 65 microns; minimum grain sizes 15 microns; average grain size, 40 microns. Grain growth increased with time during the second, or higher fire, for all firing atmospheres combinations. The rate of growth with argon was the lowest of all atmospheres. When hydrogen, oxygen, or vacuum was used during the first firing the rate of grain growth was somewhat higher for argon than for the other atmospheres after the second firing; however, the grain size for specimens fired initially in argon was less in the second fire for all atmospheres. The grain growth patterns for all specimens show fairly good correlation with specific gravity determinations; furthermore, those few specimens which showed measurable translucency values generally

exhibited largest grain size. The only evidences of exaggerated grain growth were found with those specimens which were fired in argon in their first fire.

Discussion of Results

Specific gravities after the first fire were fairly low, which may explain why no transparency was developed in the second fire. It is believed that the body must be nearly theoretically dense after the first firing if any appreciable translucency is to be developed in the second fire. A longer firing time in the first fire may be necessary. Further a rather large quantity of voids was present in most cases. Voids are detrimental to transparency as they diffract light rays passing through the body. It was found that those bodies which exhibited some degree of transparency were of low void content, 0.5% or less.

Nearly all samples were contaminated with molybdenum. In most cases the contamination was on the outside of the specimen, and most of it was easily ground off, however, most of the specimens were left with a grayish haze on the surface, which undoubtedly influenced translucency measurements. Microscopic examinations showed very few pores present for those specimens approaching true density and it is believed that the contamination had only a small effect on these measurements.

One of the most important factors causing the low degree of transparency may be the anisotropic properties of alumina which may cause light rays to be scattered in much the same way as do voids. The use of cubic crystalline phases should overcome this problem.

Summary

The object of this phase of the program was the development of transparent polycrystalline ceramics. Alumina, though an anisotropic crystalline phase, was selected for study with the approach being to utilize the procedures and knowledge disclosed for making "Lucalox", the industrial transparent polycrystalline ceramic; but further, to study the effect on varying firing atmospheres on transparency.

Alumina bodies were prepared from a substantially pure, finely-divided alumina, with a minor addition of magnesia to inhibit discontinuous grain growth. The specimens were fired to 1700°C for 100 minutes in one of four atmospheres: argon, hydrogen, vacuum, or oxygen. They were then given a second firing in each of these atmospheres respectively to 1900°C for a period of from 15 minutes to 5 hours.

Specific gravity, moisture absorption, and total porosity were determined for each set of firing conditions; translucency measurements were taken for those specimens capable of transmitt

at least 30% of the incident light; further, a microscopic examination was made of the specimens including pore size and pore location, and, grain size; and finally the microstructure was related to the other results. Specific gravities approaching theoretical were attained however the resulting transparency was less than that of Lucalox. This may be due to molybdenum contamination but more likely to the entrapped voids.

With the exception of those specimens fired in argon, all generally acquired a greater densification during the second fire when the ambient atmosphere was the same as that in which the specimen was sintered during the first fire. On the whole, however, hydrogen, oxygen, and vacuum-sintered specimens showed nearly the same results with both densification rates and grain growth. Fairly good correlation was found between densification and structure.

Final Report - Part I

TRANSPARENT POLYCRYSTALLINE CERAMICS

Section B - Isotropic Crystalline Phases

Introduction

Most effort to the present in the sintering of pure oxides and attempting to attain theoretical density has been with alumina. In general the best resulting specimen exhibits a rather high degree of transparency when the ceramic specimen is in direct contact with a surface. As the ceramic specimen is moved away from the surface the transparency quality disappears. This is the case even with General Electric Company's "Lucalox." The reason for this effect may be the anisotropy of alumina since the system in which it crystallizes is hexagonal.

Section A of this part deals with efforts devoted to alumina. The results attained are in accordance with the discussion above. The object of this phase of the work was to attempt to attain theoretical density utilizing a stable, refractory, strong, cubic crystalline phases.

Procedure and Experimental Data

Magnesium aluminates, $MgAl_2O_4$, was the spinel composition chosen to begin the cubic phase investigation. In

order to aid in the formation of the spinel and to insure very small particle size, the raw materials chosen were reagent grade ammonium aluminum sulphate and U.S.P. Magnesium sulphate which were compounded to form $MgAl_2O_4$. These materials are transformed totally into a liquid phase between 200 and 500°F. As the temperature increases, the liquid boils giving intimate mixing. With continued heating to a temperature of 1832°F and soaking until all the volatiles are driven off, magnesium aluminate spinel is formed. This is the only phase detectable by X-ray diffraction.

The calcined spinel which was very soft and fluffy was passed through a 200 mesh screen and then pressed into discs. Approximately 15% water and a pressure of 5,000 psi were used in the formation of the discs. A solution of stearic acid and carbon tetrachloride served to lubricate the die. The discs next were placed into a dryer (150°F) for a day.

The spinel discs were fired in a gas fired kiln in an air atmosphere on zirconium setters to find the maturing temperature of the spinel. The fired bulk density and the moisture absorption were measured by the water immersion method. The results were calculated by using the following formulas:

$$Db = \frac{D}{W - S} = \text{Bulk Density (g/cc)}$$

$$M.A. = \frac{W - D}{D} = \% \text{ Moisture Absorption}$$

where:

D = the dry weight

W = the wet weight

S = the suspended weight

The data and calculated results are listed in the following table, and they are shown in the Figures on page

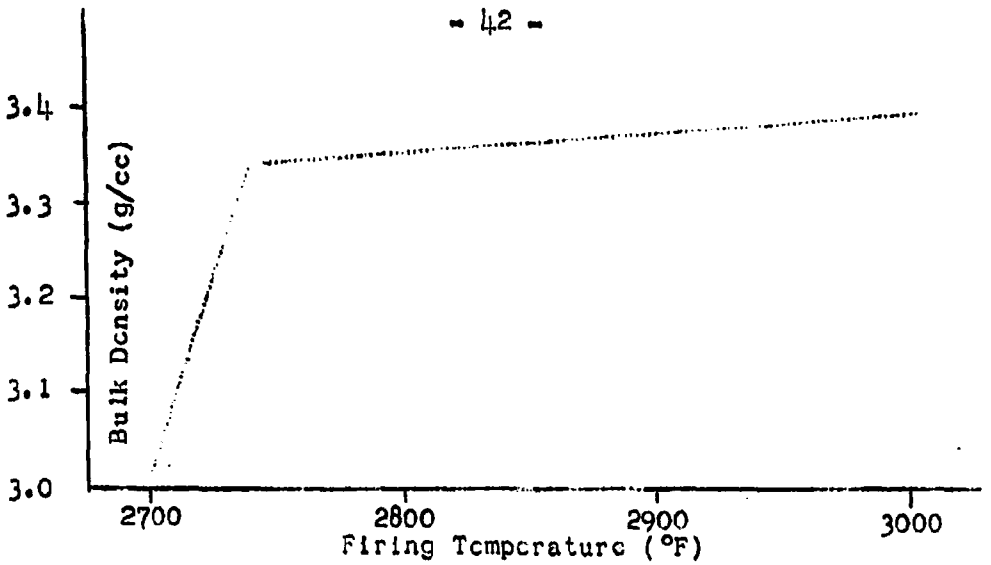
Temperature	Soak(hrs)	Bd(g/cc)	M.A.(%)
2700	1	3.042	4.95
2732	1	3.347	1.34
2800	1	3.356	0.62
2900	1	3.365	0.54
3000	---	3.389	0.05

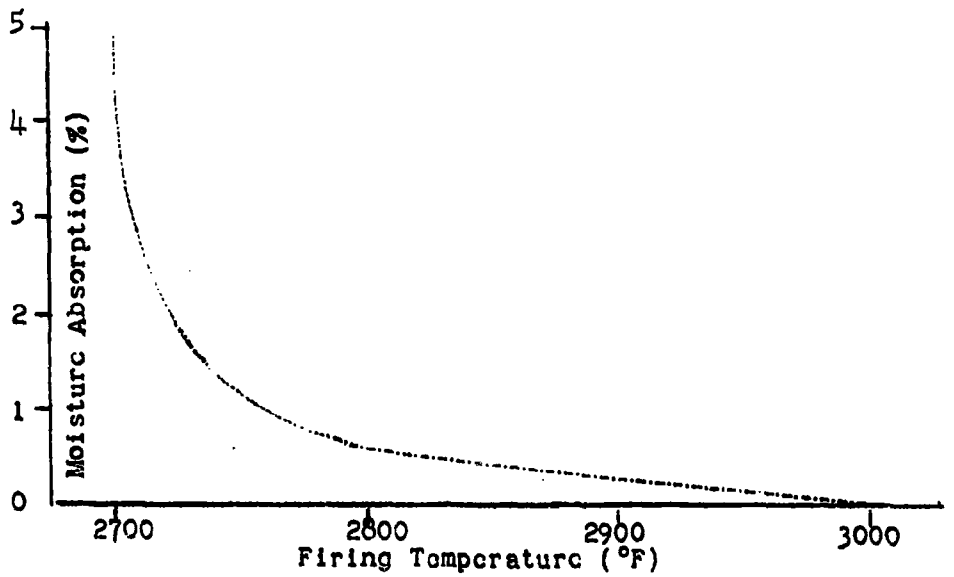
(Theoretical Density of $MgAl_2O_4$ = 3.58)

Results

As can be seen from the table, the highest density obtained was 3.389 at a moisture absorption of .05%. This density is 94.6% of theoretical density. Probably a higher density could have been obtained at longer soak times or higher firing temperatures. Also sintering studies in various atmospheres would probably have improved the density.

Bulk Density vs. Firing Temperature





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Summary

A study of the sintering characteristics of the cubic crystalline phase, namely spinel $MgAl_2O_4$, was initiated. The raw materials selected to form the compound are magnesium sulphate and ammonium aluminum sulphate (alum). On mixing in the correct proportions and calcining these compounds melt between 200 to 500°F and mix intimately. On further calculation the volitiles are dried off and spinel is formed at 1830°F. This spinel is then fabricated into specimens and fired. Firing in gas fired kiln to 3000°F results in a bulk density of 3.389 (which is 94.6% of the theoretical density) and a moisture absorption of 0.05%. Firing at increased temperatures and also in controlled atmospheres would undoubtedly result in attaining of theoretical density and a high degree of transparency.

Final Report - Part IV

LANTHANUM ALUMINO SILICATE DIELECTRICS

Object

The object of this investigation was to develop a material with a dielectric constant of 15 and power factor of 0.0005 at microwave frequencies.

Approach

The approach to this problem was divided between two systems. The first system was a study of glass-crystal composites in the lanthana-alumina-silica system. The second system comprised a study of pure ceramic compounds with the major portion being devoted to the titanates but also including the stannates.

La_2O_3.Al_2O_3.SiO_2 System

The first system evaluated was the lanthana-alumina-silica ternary. Unfortunately there was no ternary phase diagram available for this system so that little was known about the compounds within the ternary.

However, it was known that $LaAlO_3$ had a dielectric constant of 26 and a power factor of 0.003. It was thought

that by blending SiO_2 with the lanthanum aluminates both a glass and a lanthanum silicate compound would form. The effect of the glass would be a reduction of the dielectric constant and it was anticipated that the lanthanum silicate compound would give lower losses. The compositions that were evaluated are given in the triaxial in Figure 1 on page .

A. Conventional Firing

Compositions were prepared by normal methods and then fired in a gas kiln. Various compositions were evaluated for dielectric properties and were found to have properties to deserve further consideration. One such composition had a dielectric constant of 15 and a power factor of 0.0004 at one megacycle.

Many problems were encountered with this method. One of these was that the compositions all had short firing ranges. Thus, attempts to produce samples large enough for dielectrometer measurements proved unsuccessful. Furthermore, these samples all had a large percentage of glass. This large percentage of glass ($\approx$12%) would lower the dielectric constant along with changing the power factor.

Another problem encountered was due to the hygroscopicity of the lanthanum oxide. Before this oxide could be weighed, it had to be calcined to remove all the water. Before the oxide could be pressed and fired, it also had to be free of water. If it were not, there would be an evaporization of the

water during firing. This would result in the formation of voids within the body and also in the dissociation of the body. Thus to make sure that no water was present at any time during the entire process, an intricate and long fabrication process was devised. The first part of this process included calcining the oxide 24 hours before it could be weighed. After mixing, the batches were wet ball-milled for six hours, then removed from the ball-mill for six hours, then removed from the ball-mill and placed in a drier overnight. This step removed the water of mixing but did not remove the hydroxide associated with La_2O_3. When dry, the oxides were pressed into discs and then calcined at 1200°F. After each day of calcining, the discs were crushed to pass through a 200 mesh. This was done to insure intimate mixing. After the third day of calcining, the discs were crushed and then repressed into discs and fired conventionally in a gas kiln. This entire process took about 1 week.

Even though this technique by itself could not be utilized due to the problems previously discussed, it did indicate that the compositions evaluated had dielectric properties which were of interest.

B. After Fire Heat Treatment

Various samples which had been fired by conventional means appeared somewhat overfired. It was thought that by a second heat treatment, an appreciable amount of glass might

be devitrified to render lower losses and greater dielectric constants.

These poorly fired samples were refired at temperatures about 400°F below the first-fire temperature for prolonged periods of time. In each the power factor decreased appreciably going from, .0018 to .0005 in various cases. Refiring of these samples to a higher temperature resulted in an increase in the power factor to a value somewhat lower than the initial power factor. The dielectric constant showed little change with these fires.

The improvement in power factor is due to continued crystal formation or growth, resulting in tying more of the lossy ions in the crystalline phase where they contribute much less to lossiness. When the power factor starts to increase again the crystals are being dissolved resulting in a higher glass content which increases the power factor.

C. Hot Pressing

The next approach tried was that of hot-pressing the composition. The first attempts to hot-press were made using carbon dies but this led to carbon contamination within the specimens. Even though the firing temperature was below 3000°F, the contamination still occurred due to carbon in the atmosphere and loose carbon from the die wall. Besides this problem, the material was extremely difficult to vitrify. Normally, at the vitrification temperature, a composition

will form some glass, become viscous and then start to extrude. It was found that in these compositions a glass was formed approximately 200°F below the reaction temperature which made it impossible to find the correct vitrification and maturing temperature by applying pressure. Consequently, only about 1 out of 5 of the specimens that were hot-pressed come out fully reacted and fully vitrified.

Despite the fact that almost all of the specimens that were hot-pressed had a glassy sheen, most of them were not completely reacted with respect to the La_2O_3. This effect took place with only the smallest amount of free lanthanum oxide remaining. This condition gave an easy and fast way to determining whether a body was completely reacted and matured.

These measurements were made with the use of a wave guide apparatus. With this technique the power factor of these low loss samples could not be measured. The main reason for this is that only relatively small samples were able to be produced. The power factor as determined in the wave guide is the combination of the power factor of both the sample and the wave guide. In the case where the sample is large, the major part of this "total" power factor is due to the sample and the effect of the wave guide is negligible. When the sample size is decreased to the size sample that had been fabricated, the loss of the wave guide compared to the loss of sample become large. Therefore, an accurate

determination of the power factor of the sample could not be made. When the specimens were underfired they would disintegrate back into powder. This became apparent within a 24 hour period.

Various compositions that were hot pressed were measured at microwave frequencies. The results of these evaluations are given below:

Table 1

Body		Mole %	Frequency (KMc)	Temperature °F	Dielectric Constant
K15	La_2O_3	26.4	8.52	72	13.9
	Al_2O_3	65.0	9.64	72	10.15
	SiO_2	8.6	8.52	300	14.0
			9.64	300	10.35
K15 + 1	La_2O_3	26.3	8.52	72	12.2
	Al_2O_3	64.5	9.64	72	11.1
	SiO_2	9.2	8.52	300	12.45
			9.64	300	11.3
K15 + 3	La_2O_3	25.4	8.52	72	10.8
	Al_2O_3	64.1	9.64	72	9.48
	SiO_2	10.5	8.52	300	10.85
			9.64	300	9.84

D. Prereacting

The major problem encountered was the extremely short firing range that is, before the La_2O_3 could react the specimens was distorted or melted. It was anticipated, however,

that if the compositions were pre-reacted to completion, the compositions during a second fire would have an adaquate firing range. The second fire would also serve as a control upon the glass percentage and help to increase the density due to sintering of the particles.

Pellets approximately 1-1/2" high by 1" in diameter were pressed and placed into an induction furnace in which molybdenum was used as a susceptor. The pellets were then heated to a point where they were completely reacted. Although the samples were completely reacted, they were contaminated with molybdenum. A technique was devised in which an alumina tube was placed between the molybdenum lines and the pellets. The samples fired in this way were reacted and free from any contamination.

Preliminary testing was carried out on the LSA-5 composition at four pre-firing temperatures. What was determined from this investigation was that the alumina shielding technique eliminated any contamination. Further, as was anticipated, there apparently was an optimum prefire and second fire temperature which gave a low loss body. With the elimination of the impurities the results were predicible and the mechanisms understandable. Thus, this physical barrier technique was used for investigation of the remainder of the ternary system.

PLOT OF COMPOSITIONS

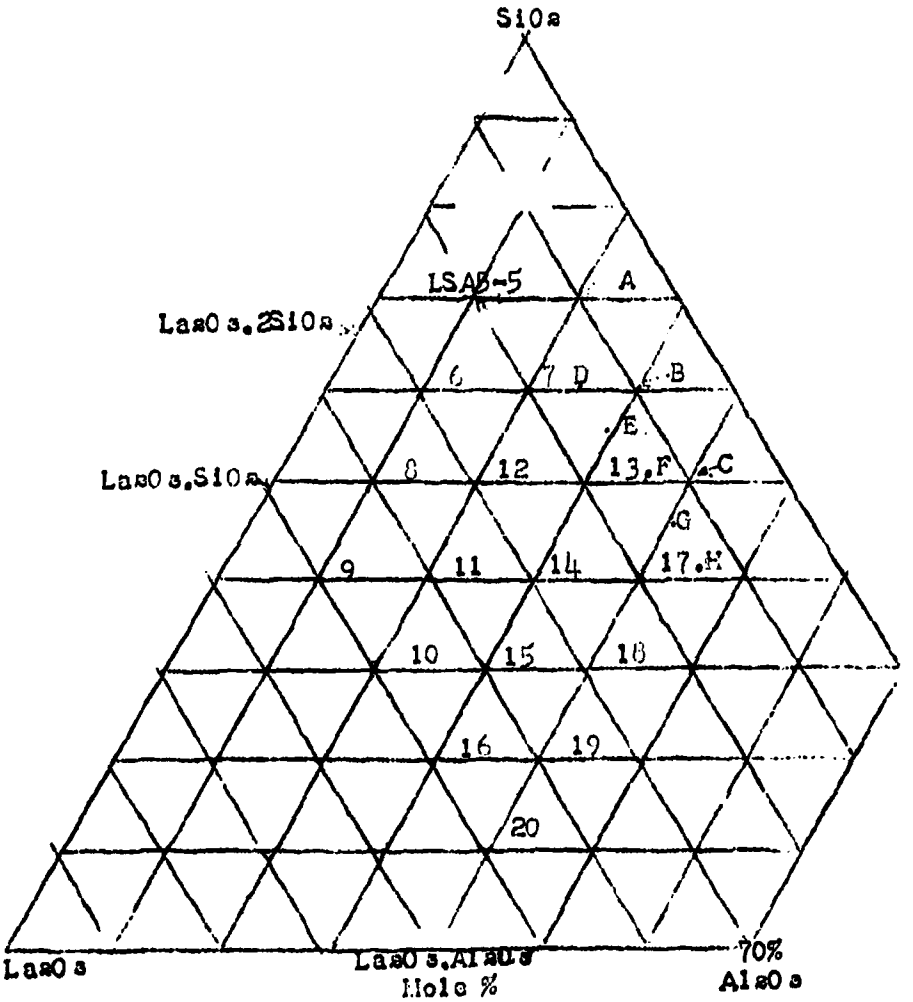

Figure I

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E. Results

The compositions that were selected are plotted in Figure 1, these compositions are in 10% increments which was deemed adequate for this study. The main reason for this was that there was no ternary compound reported for this system. Thus, all of the properties of the compositions will be relative to the properties of the binary compounds and the glass phase and their percentages within each composition. However, they will also be effected by changes in the physical structure of each body such as pore size, percentages of glass, crystals and pores grain size, and crystal size.

All of the compositions that were matured had electrical tests performed on them. For each composition, a minimum of ten samples were evaluated. The electrical properties given in Table 1 on page 53 represents some of the more consistent values obtained. Some of these values are plotted in Figure 3. Before an understanding of these results could be attained, data was needed concerning the percentages of the various phases within each composite. Therefore, a polished section was made and analyzed petrographically for each atmosphere. The results of this analysis are given in Table 2. It should be noted that only one polished section analysis was made for each composition.

The first thing to be noted is that the tan δ of compositions containing all but a small amount of $LaAlO_3$ becomes fairly high. This, of course, is understandable since $LaAlO_3$ as a single crystal has a loss of 0.0033 and so its contribution to a polycrystalline composite will raise the losses

TABLE 1

Dielectric Properties of Compounds

Composition	Sample No.	Pre-fire (°F)	Re-fire (°F)	Soak (Hr.)	Kiln #	K	Tan δ (%)	Bulk Density	Moisture Absorption (%)
5	9_1	2535	2160	2	1	7.82	0.092	3.83	0.01
	9_2	--	2120	3	1	7.84	0.062	3.85	0.00
	4	--	2200	7	2	7.70	0.135	3.70	0.05
	13	--	2140	11	2	7.75	0.080	3.78	0.01
	7_1	--	2220	3	2	7.68	0.061	3.83	0.00
	7_2	--	2160	9	2	7.78	0.053	3.84	0.00
6	7	2600	2600	1	3	7.67	0.092	4.23	0.04
	8	2600	2620	1	3	7.68	0.075	4.24	0.03
7	5	2440	2420	1	1	7.08	0.081	3.70	0.06
	15	--	2320	16	2	7.00	0.087	3.68	0.04
8	5	2700	2710	1	3	10.03	0.123	4.76	0.04
	6	--	2710	1	3	10.14	0.124	4.78	0.03
11	5	2700	2800	1	3	12.30	0.156	5.15	0.08
	1	--	2820	1	3	12.40	0.132	5.18	0.06
12	12	2650	2680	1	3	9.53	0.242	5.19	0.08
	14	--	2660	1	3	9.53	0.250	5.11	0.07
13	2	2460	2460	1	2	8.12	0.067	3.73	0.00
	6	--	2430	2	2	8.40	0.095	3.71	0.01

TABLE 1 (Cont.)

14	3	2580	2620	1	3	11.32	0.232	4.32	0.08
	5	--	2620	1	3	11.50	0.255	4.38	0.07
15	6	2600	2760	1	3	12.08	0.375	5.05	0.02
	5	--	2740	1	3	12.95	0.314	5.03	0.01
17	6	2650	2590	1	3	8.32	0.090	3.65	0.01
	7	--	2600	1	3	8.73	0.093	2.67	0.01
18	3	2650	2760	1	3	10.30	0.324	4.87	0.05
	4	--	2780	1	3	10.00	0.387	4.85	0.12
19	4	2750	2840	1	3	13.38	0.386	5.50	0.10
	6	--	2840	1	3	13.50	0.345	5.58	0.09

* 3 Denotes Gas Kiln

1 Denotes Glo-Bar Furnace

2 Denotes Platinum Wound Furnace

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ELECTRICAL PROPERTIES OF COMPOSITIONS

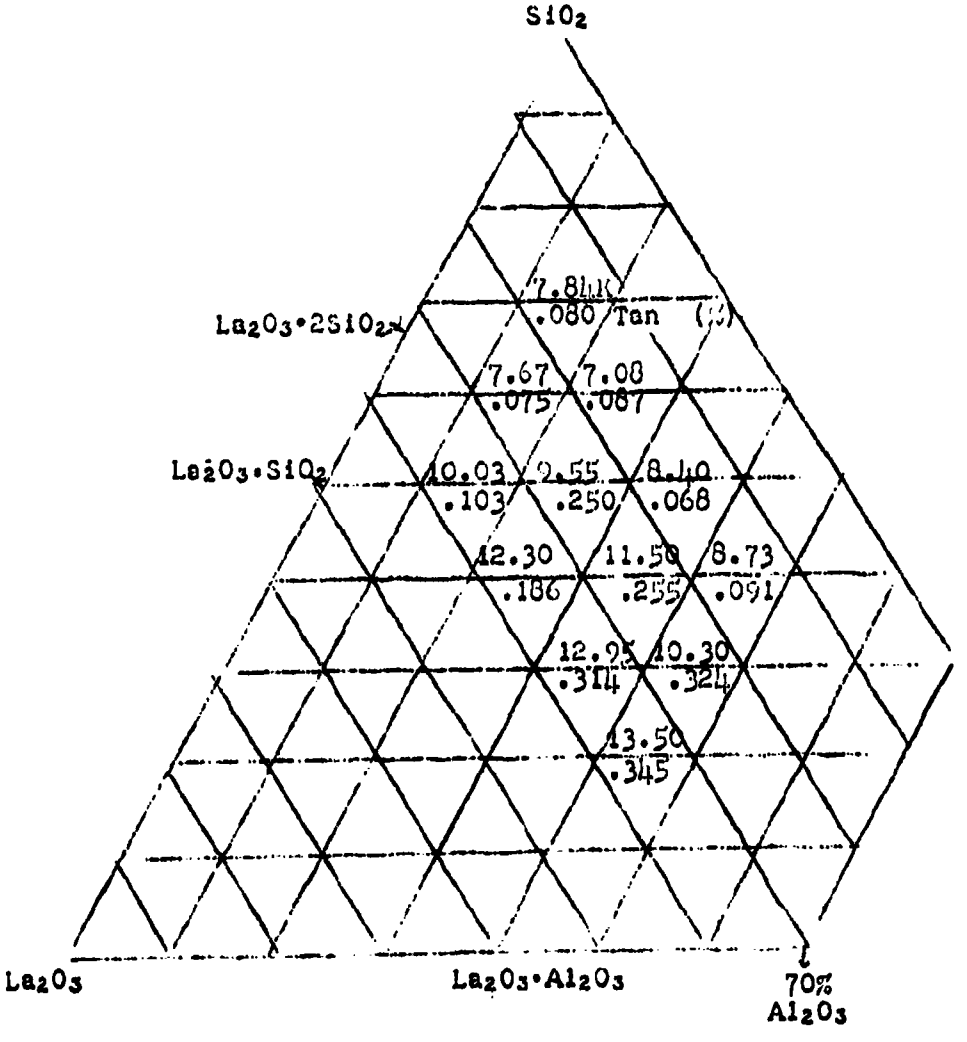

Figure 2

TABLE 2.

Phase Analysis of Compounds

Composition	Sample No.	Void (%)	La_2Si_2O	*	La_2SiO_5	$LaAlO_3$	Unknown	Glass (%)
5	9₂	1	80					19
6	7	4		59		20		17
7	5	6		76				18
8	6	5		57		21		17
11	5	6		37		40		17
12	14	11	39			37		13
13	6	5			57		12	16
14	5	8	30			47	3	12
15	5	11	10			67		12
17	7	4			55		23	17
18	3	11	11			63		15
19	6	9				70		12

* No determination made between $La_2Si_2O_7$ and La_2SiO_5 crystals.

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if the body is initially low loss. Also adding another crystalline phase to the system might allow far more structural defects leading to loss.

$La_2Si_2O_7$ had been reported as having a dielectric constant of 10 and a tan δ of 0.0002 (Report No. 5). The La_2SiO_5 composition had not been investigated. The composition had a pre-firing temperature of over 3400°F and so it was prepared by hot-pressing the composition in graphite dies. The slug which was produced was vitrified but contained a considerable amount of carbon contamination. The dielectric constant of it was 12.68 and the tan δ was .0012. Since the slug was contaminated, the losses and the dielectric constant would be higher than it would be if it were free from impurities. These results did, however, indicate that this crystalline form of La_2SiO_5 had a higher dielectric constant then the $La_2Si_2O_7$ (Report No. 5). Since this type of contamination would affect the losses to a greater degree than it would affect the dielectric constant, little could be determined about the power factor of the La_2SiO_5 composition except that it was fairly low loss. The two compositions containing only $La_2Si_2O_7$, 5 and LSA-5, had the lowest losses. Composition #13 which consisted of 67% La_2SiO_5 with 12% of the unknown crystalline phase had loss values as low as either composition 5 or LSA-5 indicating the low loss characteristics of La_2SiO_5.

Instead of correlating the measured dielectric constant values, they were corrected for porosity after measurement

and then correlated. It has already been explained that the presence of pores has the effect of lowering the dielectric constant. Applying the logarithmic rule to correct for these pores resulted in a new series of dielectric constant values. This set of values along with the observed values are plotted in Figure 32. The change in the dielectric constants after the corrections is appreciable.

If the amount of La_2O_3 is held constant and SiO_2 is replaced by Al_2O_3 the dielectric constant increases in all but one case. On the low La_2O_3 side of the diagram, composition #5 contained only $La_2Si_2O_7$ and thus gives a low dielectric constant. Moving to composition #7, there was a decrease in $La_2Si_2O_7$ with the presence of a small amount of $LaSiO_5$ which had a higher dielectric constant. The exact amount of $LaSiO_5$ could not be determined in any of the compositions since this compound and $La_2Si_2O_7$ appeared indistinguishable in polished sections. Although the difference between the dielectric constants of #5 and #7 should be larger, it must be realized that with only one polished section on which base the analyse there may be minor discrepancies in the results. Compositions 13 and 17 showed increased dielectric constants since the amount of $LaSiO_5$ had increased with the disappearance of $La_2Si_2O_7$ and the appearance of an unidentified compound. In the region of a moderate amount of La_2O_3 the same increase of dielectric constant upon the replacement of Al_2O_3 for SiO_2 occured. This is due to the increased percentage of $LaAlO_3$ compound.

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CORRECTED VALUES OF DIELECTRIC CONSTANT

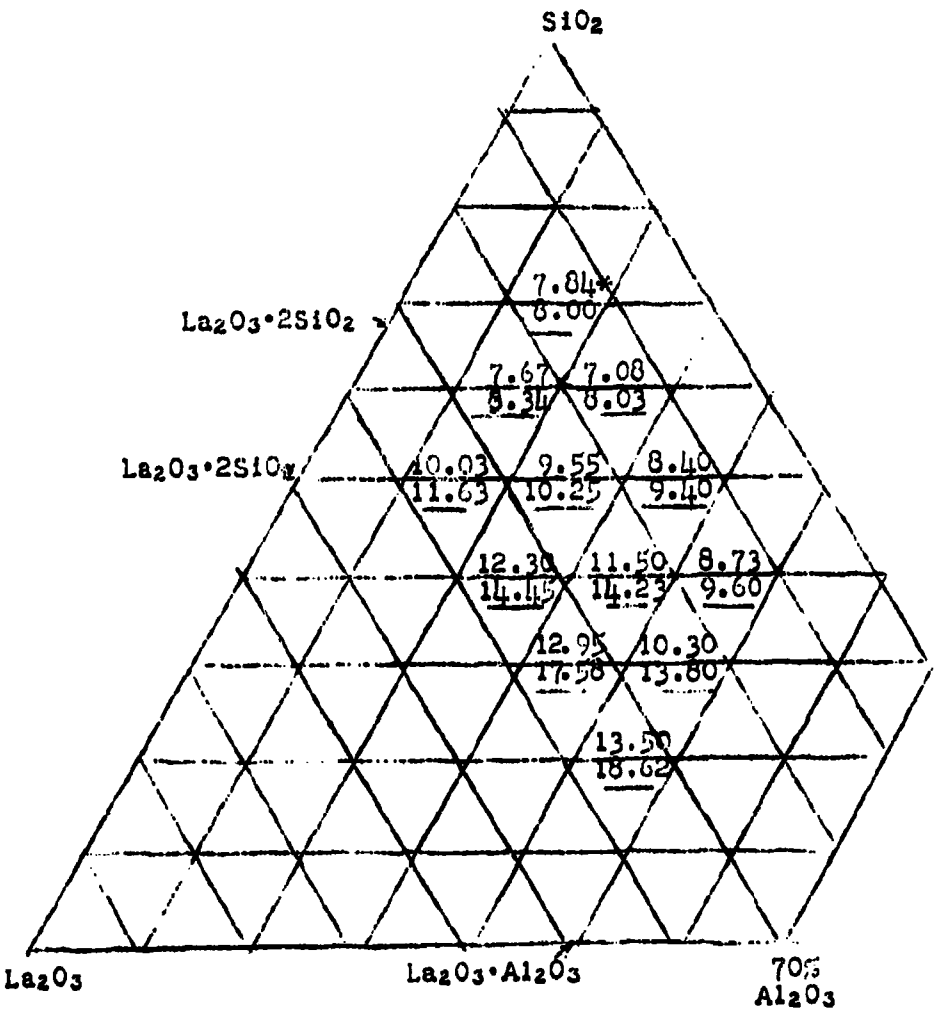


Figure 3

* Top number is recorded value while lower number which is underlined is the corrected value.

An exception occurs between compositions #14 and #18 in which there is a decrease in dielectric constant with an increase in $LaAlaO_3$. The obvious reason for this effect is that composition #18 has 3% more glass than #14 and also there is a trace amount of the unknown compound in #14 which may have the effect of slightly raising the dielectric constant. With the compositions high in La_2O_3, this trend of increasing dielectric constant with increasing Al_2O_3 percentages holds true. There is again an increasing amount of $LaAlO_3$ in the compositions.

This same trend can be explained if the Al_2O_3 content is held constant and SiO_2 is replaced by La_2O_3. In all cases the dielectric constant will increase with increased amounts of La_2O_3. This is the same explanation as before: with increased amounts of La_2O_3, the content of the low dielectric constant lanthanum silicate is being replaced by the higher dielectric constant crystalline phase $LaAlO_3$.

The correlation of the tan δ throughout the system has a similar trend connected with it. Whenever either of the lanthanum silicates are the major crystalline phase, the body will exhibit low losses. With the introduction of $LaAlO_3$ the losses will jump appreciably with only one composition, #6, showing low loss with a substantial amount of $LaAlO_3$. With increased amounts of lanthanum aluminate, the losses will show a continued increase. The trend ceases when comparing the losses on the low La_2O_3 side of the ternary. As was shown

with the LSA-5 composition, the amount of glass is important when comparing the losses of the bodies. The composition with the lowest loss, #13, also has the smallest amount of glass and the most uniform distribution of the glass phase. All of these compositions were crushed in an iron mortar after the pre-reacting fire. The presence of iron contamination is another reason why the losses are not as low as the LSA-5 composition, besides the fact that they contain more glass than LSA-5.

Various fabrication methods had been tried. Calcining the material and then firing it conventionally proved very difficult and inconsistent. Hot-pressing gave vitrified bodies but the slugs were highly contaminated with carbon and when they were formed with molybdenum layers, they contained molybdenum contamination. Except for the $LaSiO_5$ compound which by necessity was hot-pressed, none of the compositions were evaluated which had been hot-pressed. The technique which gave reliable results was the pre-reacting technique using aluminum shielding. After the bodies were prereacted they contained no contamination. The only contamination within the compositions, other than the impurities within the starting oxides themselves, was from the crushing operation which introced a portion of iron contamination which could not be completely removed.

Four prefiring temperatures were employed with the LSA-5 composition. The lowest loss and the highest diclectric

constant material occurred with the 2600°F prefiring temperature. This composition contained the lowest amount of glass ($\approx$ 12%) with this glass phase being fairly evenly distributed throughout the body. Since this composition may have contained small amounts of iron impurity it would appear that lowering percentages of the glass phase would decrease the losses. The reason for this was that the iron would be more mobile in the glass phase since it was being held less tightly than if it were in the crystal phase. Material fired to 2900°F and 2975°F were crushed in iron and in alumina. Although too few samples were prepared to make an absolute statement, the lowest losses were observed in the compositions free from iron and with a slightly higher amount of glass. The conclusions from this experiment were that with iron impurities, the glass phase contributed larger losses than the crystal phase at 1 megacycle but with the elimination of the contamination, the glass phase exhibited losses comparable to the crystal phase. Although the losses exhibited by the 2900°F and 2975°F fires were not as low as the 2600°F fire, this could be explained by the higher percentage of the glass phase in the higher fires. This would have the effect of allowing any impurities greater opertunity of entering the glass phase where they would have greater mobility than in the crystalline phase.

The other compositions evaluated in the system had consistent values. The dielectric constant increases along with the tanδ on the introduction of the $LaAlO_3$ phase. The losses

exhibited by the compositions free of any $LaAlO_3$, namely 5, 7, 13, and 17, were quite low. This is understandable since both La_2SiO_5 and $La_2Si_2O_7$ exhibit low losses. A complete explanation of the variations between these four could not be presented since the exact loss of the La_2SiO_5 phase was not known.

An unidentified crystalline phase occurred in three of these compositions. The X-ray diffraction data recorded for this crystalline phase did not conform to any data published on the three binary diagrams. Thus it appeared that a ternary composition existed. Investigations of various compositions in this area indicated that with the introduction of this crystalline phase, the firing temperatures of the compositions were increased. This condition does not allow this compound to be explained as a ternary composition. Before a positive statement can be made more work would have to be performed over a wider compositional area with the object being to isolate this compound and then analyze it.

F. Summary

1. The pre-firing procedure using an alumina shielding technique appears to be the best method for fabricating the lanthanum compositions.

2. The amounts of iron picked up in grinding could not be completely removed by passing the material over a magnet.

It appears to have detrimental effects on the Tanδ but not to a marked degree.

3. The occurrence of lanthanum aluminate in the compositions had the effect of raising both the dielectric constant and the power factor.

4. The electrical properties of compositions within the ternary system are predictable on the basis of crystal phases and content and glass content.

5. The glass could not be substantially devitrified to give a high crystal percentage.

6. Results observed in this sytem indicated that the dielectric properties of this type composition does not fulfill the requirements of the contract.

Crystalline Dielectrics

A. Introduction

Various systems have been evaluated which contain no glass. Those which gave the best results were the titanates and the stannates.

B. Magnesium Titanates Zirconates

In the quest to fulfill the technical requirements of this problem, compositions, within the system MgO - ZrO$_2$ - TiO$_2$ were evaluated. The two compositions which gave the

best results have the molecular ratios of 2-1-2 and 4-1-4.

These oxides were weighed according to formula and then ball-milled for six hours using ethylene dichloride as the dispersant. The batch was then dried overnight. Discs were pressed and then fired conventionally. The samples were fired to various temperatures and at soak times until the combination which gave the optimum density was determined. After the discs were matured, they were machined to size and tolerances for the determinations of electrical properties, power factor and dielectric constant, at 8.6 KMc in a microwave dielectrometer.

The properties of compositions 2-1-2 and 4-1-4 at 1 Mc and 8.5 KMc; absorption, etc of these composites and other results are given in Table 3 on page 66.

Thus it was apparent that both compositions were somewhat affected at high frequencies. The cause of this phenomenon is normally attributed to impurities. However, the low and microwave frequency measurements were determined by different instruments. This, in itself, might be the cause of the change in electrical properties.

C. Calcium Stannate

High purity calcium stannate was obtained from Metal and Thermit Company. The compound was pressed into discs and calcined at 1060°C with a two hour soak. The discs were then crushed to pass 200 mesh. The screened material was

Table 3

Electrical Measurements

Composition 2-1-2

Firing Temperature	Soak (hrs.)	1 Mc.	8.5 Mc.	1 Mc.	8.5 Mc.
2790*	1	18	17.2	.0006	.0018
2790	1		19.2		.0022
2790	1		19.6		.0020
2810	1		18.1		.0016
2810	1		18.65		.0019
2810	1		17.1		.0020
2810	1		18.3		.0020

Composition 4-1-4

2800	2	18.0	17.9	.0005	.0019
2800	2		17.65		.0016
2800	2		19.65		.0021
2800	2		18.1		.0020
2800	2		17.5		.0017
2800	2		20.5		.0024
2800	2		17.9		.0020
2800	2		17.65		.0019

* All these samples had 0.0% moisture absorption.

then mixed with a 5 weight mixture of AoT (5%) and water. This combination served as both a lubricant and a binder. This material was pressed into discs and fired to maturity at 1430°C.

The dielectric properties of this compound at 1 Mc. are given in the table below

	°C	K	P. F.
	1430	14	.0004
$CaSiO_3$	1440	14.3	.0004

Measurements were not made at the microwave frequencies since samples could not be fabricated large enough to give accurate results when used in the wave guide apparatus. Consequently, microwave measurements were not made.

D. Commercially Available Material

As noted in Progress Report No. 7 on page 41, dated May 1 to August 1, 1963, it was learned several months ago that Trans-Techn, Inc. of Gaithersburg, Maryland, has developed a ceramic which appears to have met the requirements of this problem. It was identified as DA 14 and had a power factor of .0004 and a dielectric constant of 13.3, however it was slightly porous. Some time later it was learned by private communication that the short coming had been eliminated and that the new material was identified as DA-15. Its power factor is .0004 or lower and its dielectric constant is 15.4.

This firm is continueing their efforts striving for dielectric constants of 20 and higher.

E. Summary

Both magnesium titanate zirconate and calcium stannate gave results at 1Mc. that were low loss with an adequate dielectric constant. When measuring magnesium titanates at the microwave frequencies, the dielectric constant remained fairly constant while the power factor rose by a factor of 3 over those measured at 1 Mc. Using conventional methods, then, to fabricate magnesium titanate did not satisfy the contract requirements. However, the requirements of this contract appeared to have been met by the results given by Trans-Tech, Incorporated.

Final Report - Part V

HOT EXTRUSION

Introduction

The objective of this program is the rapid hot extrusion of ceramic materials to produce a product having the high per cent of true density and small crystal size which can be obtained by hot pressing. The successful development of hot extrusion procedures should permit higher productivity and, it is hoped, greater design flexibility than can be obtained by hot pressing.

Work performed by Nuclear Metals, Incorporated demonstrated the feasibility of coextruding a ceramic material within a metal sheath.[1] The metal is visualized as a lubricant for the extrusion

To obtain some indication of the possibility of coextruding barium titanate in a steel sheath, a few preliminary extrusion attempts were performed at Extrusions, Inc., Caldwell, New Jersey.[2] Although only three trials were performed, the following tentative conclusions were reached.

---

[1] J. G. Hunt and P. Lowenstein, "Fabrication of Clad Massive UO_2 Fuel Elements by Coextrusion" Fourth Quarterly Report, Contract No. AT(30-0)-1565, Nuclear Metals, Inc., Concord, Massachusetts, June 6, 1960.

[2] "Development of Ceramic Dielectrics," Progress Report No. V, Contract No. DA-36-039-sc-78084, Rutgers, the State University, New Brunswick, New Jersey, December, 1959.

1. Barium Titanate having high density and small crystal size can be coextruded in a metal sheath.

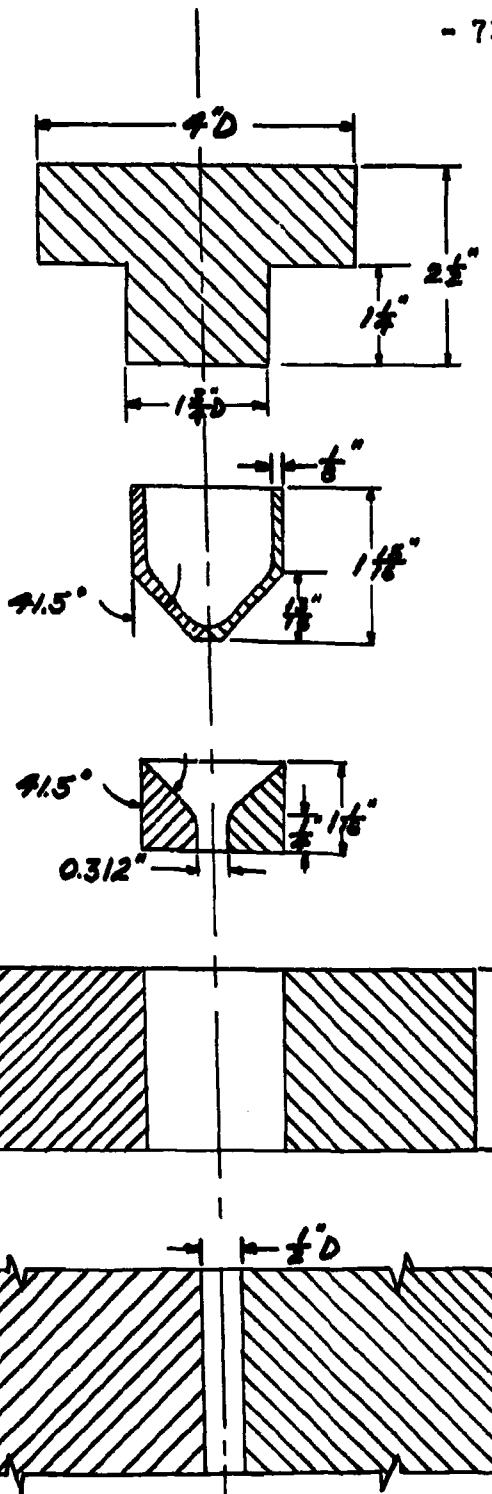
2. The electrical properties of this material are essentially the same as those of hot pressed material.

3. Even when extrusion did not occur, the barium titanate exhibited the same properties as the hot pressed material.

Following this preliminary work, a facility was established at Rutgers for study of hot extrusion of ceramic materials. An exploded view of the essential components of the extrusion assembly used in this work is shown in Figure 1. Coextrusion can and extrusion die design have been modified as work progressed. The press used is an electrically operated, hydraulic, 150 ton capacity, constant pressure Dake Press, Model No. 21-150. The maximum ram speed is approximately 17 inches per minute.

In use, the extrusion barrel with the die in place rests upon the base plate. It is positioned on the base plate directly under the ram and over a hole to allow the extruded rod to pass through the plate. The positioning of the barrel is accomplished by pushing the barrel firmly against two pins set tangentially along the circumference of a circle having the same diameter as the barrel. The

Figure 1
Exploded Cross Section of
Hot Extrusion Assembly



Extrusion Ram
Heat treated 4140 steel,
Rockwell C40-45

Coextrusion Can
O.D. approximately 1.70",
depends on expansion of
metal and extrusion
temperature

Extrusion Die
1-3/4" O.D.
Heat treated 4140 steel,
Rockwell C40-45

Extrusion Barrel
6-1/2" O.D., 1-3/4" I.D.
Heat treated 4140 steel,
Rockwell C40-45

Base Plate
24" x 18"

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angular distance between the pins is approximately 100°.

The extrusion ram is placed on top of the extrusion barrel and off to one side enough so that it is clear of the inside diameter of the barrel. The press ram is then run down until it is only a fraction of an inch above the top of the extrusion ram.

The coextrusion can and the ceramic material to be extruded are heated, either separately or together depending upon temperature requirements, and are then quickly placed in the extrusion barrel. Then the extrusion ram is slipped into the barrel and the press ram brought down as quickly as possible.

Resume of Work Performed

To test equipment, materials which were known to extrude with relative ease were first tried. Solid billets of Type 1100F aluminum were extruded at room temperature and an extrusion ratio of 32:1.

Coextrusion of a powdered glass-mica material[3] in both 1018 steel and 1100 aluminum cans of the design shown in Figure 1 was attempted at a number of different temperatures.

[3] This was a glass-bonded mica composition supplied by Molecular Dielectrics, Clifton, New Jersey. This composition can be transfer molded.

Temperatures of up to 1700°F were used with the steel cans and no extrusion was accomplished.

The attempts to extrude the glass-mica material in the aluminum coextrusion cans demonstrated that these materials could be extruded. However, the glass-mica material ruptured the extruded portion of the aluminum in every case. This occurred even when the coextrusion can was not heated and the glass-mica material was heated to 1100°F.

This problem was overcome by making coextrusion cans having 3/8" rather than only 1/8" thick walls. Cross-sections of the extrusions obtained with the thick and the thin walled coextrusion cans are shown in Figure 2.

Several attempts to extrude solid 1018 steel and Monel metal billets were not successful at the maximum pressure capacity of the press using the 32:1 extrusion ratio. Therefore, extrusion dies having 10:1 and 5:1 extrusion ratios were made.

Successful extrusion of solid 1018 steel billets were accomplished using a 5:1 extrusion ratio die with the billet having been heated to 2200°F and the barrel and die to 400°F.

A number of attempts were made to extrude both lead zirconate titanate and barium titanate in 1018 steel cans of the design which worked successfully in the aluminum-glass-mica extrusion. In one of these attempts a successful extrusion was achieved. However, attempts to duplicate

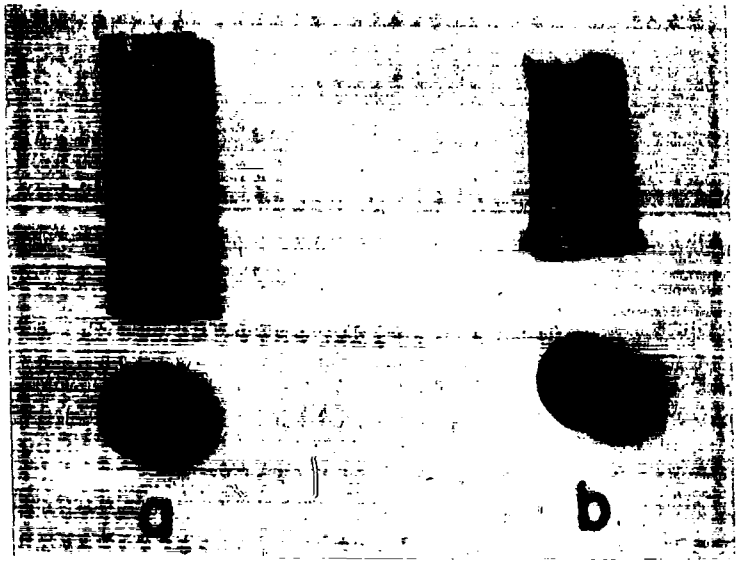

Figure 2

Cross-Sections of Glass-Mica Material
Extruded in: (a) Thick and (b)
Thin-Walled Aluminum Coextrusion Cans

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this extrusion were not successful. A cross-section of the successful extrusion is shown in Figure 3. The ceramic material is dense but extrusion was not uniform.

It appeared that the pressure needed for extrusion with the designs being used was so close to the maximum pressure limitations of the press that conditions had to be exactly correct to allow extrusion. Any small variations in conditions resulted in no extrusion.

Since it was possible to readily extrude solid steel billets, it was believed that it was the ceramic itself which was defeating the extrusion. Thus it was decided to modify the design of the coextrusion cans. The two modified can designs used are shown in Figures 4 and 5.

The type 7 can was visualized as a design for which the original pressure needed to begin extrusion would be lower since there would not be a large amount of ceramic in the forward end of the extrusion. In this design there is a large amount of metal which should start extruding before the ceramic, followed by a gradually increasing amount of ceramic. Since it is well established that the original upset pressure for extrusion is always considerably higher than that needed to continue extrusion after upset, it was hoped that the large volume of metal in the forward end of this design would help to keep the pressure needed for upset within the range of the equipment being used.

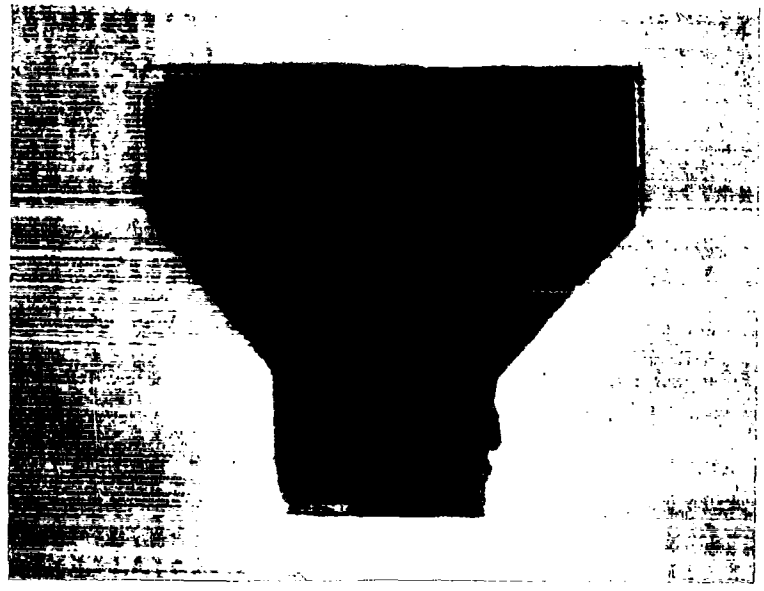

Figure 3

Cross-Section of Lead Zirconate Titanate
Extruded in a 1018 Steel Coextrusion Can

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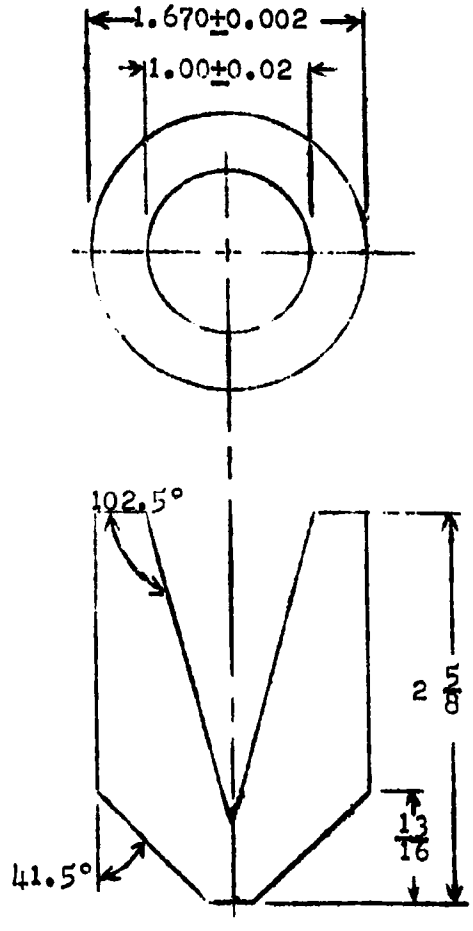

Figure 4

Cocxtrusion C_an - Type 7

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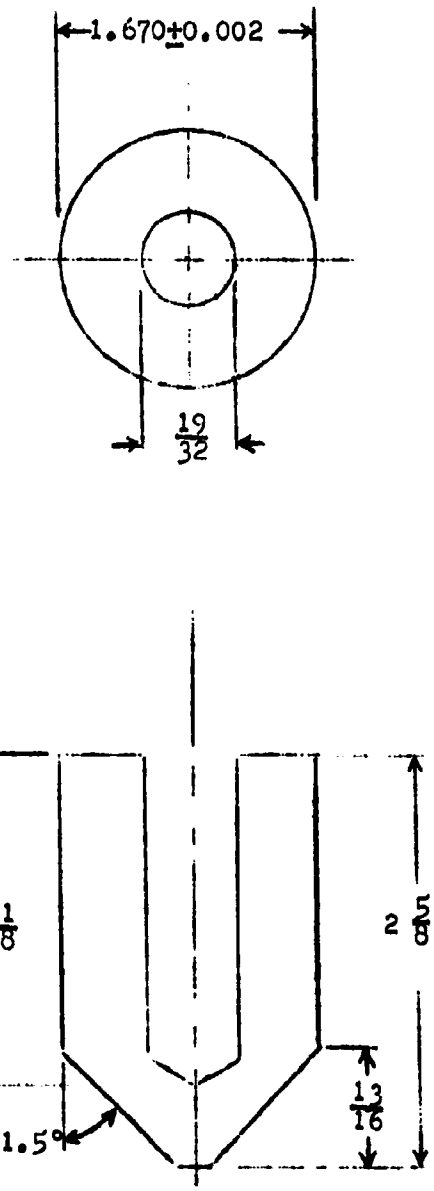
Figure 5



Coextrusion Can - Type 8

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The Type 8 Coextrusion Can was designed so that the diameter of the ceramic portion would be approximately the same as the diameter of the extrusion die. This is a considerable decrease in the volume of ceramic material used in previous can designs and should make extrusion easier.

Extrusion trials were performed with both Type 7 and Type 8 cans using $BaTiO_3$ as the ceramic portion. In all cases the ceramic powder was packed in the can at room temperature and approximately 2000 psi. Then the packed cans were heated to 2250°F, soaked for 1/2 hour, and extruded using a 5:1 extrusion ratio. Both types of billet were successfully extruded at 110,000 psi. However, when these specimens were cut open for examination, it was found that the extrusion of the ceramic material was discontinuous. The ceramic had started to extrude with the steel so that the first portion of the extrusion contained ceramic material, but the latter portion of the extrusion was solid steel. This discontinuous extrusion of the ceramic may have been caused by the ceramic material not being dense when extrusion commenced. This is visualized to happen in the following manner. The original movement of the extrusion ram produces a pressure on the steel coextrusion can forcing it to start to extrude. However, if the ceramic is not dense, the pressure from the extrusion ram will start to densify the ceramic but will not be totally transmitted to the furthermost

portion of the ceramic. Thus the forward portion of the steel which is starting through the extrusion die could carry some of the forward portion of the ceramic along with it while the rear part of the ceramic remains essentially stationary. Once the break in the ceramic portion occurs the advancing steel, as it enters the conical entry angle of the die, is forced inward to occupy the space between the two sections of the ceramic material. Sections from the two extrusions are shown in Figures 6 and 7. The ceramic portion of the extruded material from the extrusion attempt with the Type 8 coextrusion can does not exhibit a 5:1 reduction ratio and much of it somewhat porous.

Summary

Attempts to rapidly hot extrude ceramic materials have indicated that extrusion is feasible at high pressures. Extrusions of barium titanate and lead zirconate titanate in steel coextrusion cans have been accomplished at pressures of slightly below 125,000 psi which is the maximum obtainable using the present press and extrusion billet size. The quality of these extrusions is not optimum. Successful extrusion with these materials and at these pressures appears to be greatly dependent upon coextrusion can design.

Figure 6

Cross-Section of Barium Titanate

Extruded in a Type 7 Coextrusion Can

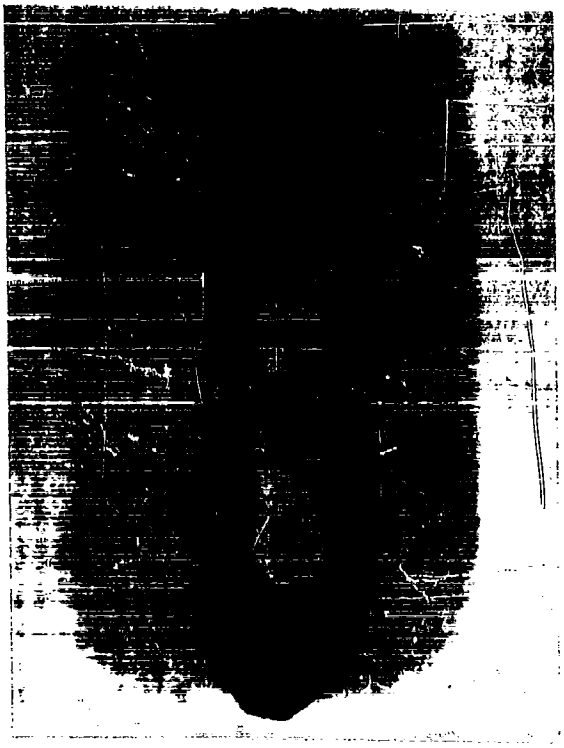

Figure 7

Cross-Section of Barium Titanate

Extruded in a Type 8 Coextrusion Can

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The effect of higher extrusion pressures will be investigated in future work along with further experimentation on coextrusion can materials and design.

SCHOOL OF CERAMICS, RUTGERS, THE STATE UNIVERSITY, New Brunswick, New Jersey INORGANIC DIELECTRICS RESEARCH by J. H. Koenig, E. J. Smoke, E. L. Kastenbein, D. A. Lupfer, et al. FINAL REPORT, U. S. ARMY ELECTRONIC RESEARCH AND DEVELOPMENT LABORATORY, Contract DA-36-039-sc-89141, November 1, 1961 to October 31, 1963.

Unclassified Report

Under Devitrified Barium Titanate a dielectric has been produced whose crystal size in the range 0.2-0.5 microns, by devitrification of a controlled finely divided $BaTiO_3$ glass. The devitrified phase is more tetragonal than normal $BaTiO_3$ and the resulting bodies exhibit a Curie temperature of 150°C. Under Low Loss Boron Nitride Dielectrics an assessment of available ceramics is presented along with a procedure developed to produce hot pressible material. A study of additives to improve the properties is presented. Under Transparent Polycrystalline Ceramics a study of the affect of combinations of firing atmospheres using a two fire procedure is presented. The atmospheres are hydrogen, oxygen, argon and vacuum. In order to increase transparency, cubic magnesium aluminate was studied. Under low Loss Dielectrics the objective is a dielectric constant of 12 and a power factor not to exceed 0.0004. The system La_2O_3-Al_2O_3-SiO_2 resulted in attaining the former requirement however the latter was not realized. The properties of several glass free compositions are also reported. Under Hot Extrusion a review of all the work is presented, including compositions, die designs, co-extrusion systems, etc. The most promising results were attained with barium titanate and lead zirconate titanate.

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